VOL. XIX. FEBRUARY, 1897. NO. 2.

AMERICAN

CHEMICAL JOURNAL.

A CONTRIBUTION TO THE STUDY OF WATER SOLUTIONS OF SOME OF THE ALUMS.[1]

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Introduction.

When a solution of a mixture of two salts having a common ion is subjected to crystallization, the two salts may either crystallize out separately or crystals may form containing both. In the latter case two modes of separation are to be distinguished, according as the crystals formed are of variable or of constant composition. When of variable composition they are mixed crystals, or isomorphous mixtures. When the constituent salts are present in constant molecular proportions, the crystalline compound is a double salt. The constancy of the composition of the crystals of a double salt raises the question whether the double salt is present as such in solution or is formed only at the moment of crystallization.

The question of the existence of double salts in solution has attracted the attention of many investigators, and a variety of methods have been used in obtaining light upon it. The most important of these are grouped according as they have to do with (a) the diffusion, (b) the thermal changes, (c) the

[1] From the dissertation of E. Mackay, Johns Hopkins University, June, 1896.

volume changes, (d) the solubility, (e) the electrical properties, or (f) the cryoscopic behavior of solutions of the compounds investigated.

Diffusion.

Graham,[1] in his classical researches on diffusion, studied incidentally the diffusion of a few double salts, among them being ordinary alum and the double sulphate of magnesium and potassium. He found that the constituents of the former were present in the diffused liquid in a proportion different from that in the alum itself, and inferred that the alum was at least partially decomposed in water solution. Graham found that the amount of the second double salt which diffused over was equal to the sum of the amounts of its constituents which diffused, when taken separately. He concluded that this double salt was not decomposed in solution.

Since Graham did not determine the proportion in which the constituents of the double sulphate of magnesium and potassium had diffused, but only the total amount diffused, his work was repeated by Marignac,[2] who, from an extensive series of observations, concluded that there is no difference in diffusion between mixtures of salts capable of forming double salts and those in which no union can take place. He inferred that double salts are formed only at the moment of crystallization.

The work of van der Wal,[3] who studied the diffusion of alums and other double sulphates, and of Ingenhoes,[4] who investigated barium acetonitrate and similar salts, lead to the same result. The latter found that the constituents of the salts examined diffused not in the proportion in which they existed in the double salt, but nearly as if they diffused separately. Rüdorff,[5] following the same mode of investigation, divided double salts into two classes according as the constituents were found in the diffusate in the same proportion as in the double salt, or in a different proportion. Rüdorff

[1] Phil. Trans., Lond., 1850, 1. [2] Ann. chim. phys., [5], **3**, 546.
[3] Inaugural Dissertation, Leyden, 1869. [4] Ber. d. chem. Ges., **12**, 1678.
[5] *Ibid.*, **21**, 4, 1882, 3044; **23**, 1846.

also investigated the relation between decomposition and concentration and found that, until near the point of saturation, the two were independent; but if crystals of the double salt were placed upon the diaphragm so as to maintain saturation, the proportion in which the constituents diffused approached much more nearly their proportion in the double salt. He concluded that molecular compounds exist in fully saturated solutions.

This conclusion was criticised by Ostwald[1] and later by Trevor[2] on the ground that the effect observed was due to the more rapidly diffusing constituent becoming relatively less concentrated in the diffusion vessel. The latter undertook a series of experiments, the result of which was to confirm this view.

On the other hand, E. Fischer and Schmidner[3] allowed a saturated solution of ferrous ammonium sulphate to diffuse upwards through rolls of filter paper inside of a glass tube, and found that the proportion of the constituents in the filter paper was the same as in the double salt.

Thermal Changes.

Thermal data, in so far as they lead to a conclusion in reference to the existence of double salts in solution, are summarized thus by Berthelot.[4] "Everything indicates that double salts formed with a *feeble* disengagement of heat are to be regarded as separated in greater part into their constituents, by water." Favre and Valson,[5] on finding that the constituents of the alums evolved no heat on mixing, concluded, as would Berthelot, that the latter came into existence only through crystallization.

Graham[6] had previously made similar experiments with other double sulphates, and had reached the same conclusion. He found, on the other hand, that thermal changes occurred when solutions of the chlorides of mercury and ammonium were mixed. Berthelot[7] observed in general that the thermal changes produced by mixing solutions of the halogen salts of

1 Ztschr. phys. Chem., **3**, 601.
2 *Ibid*, **7**, 468.
3 Ann. Chem. (Liebig), **272**, 156.
4 Méc. Chem., II, 324.
5 Compt. rend., **74**, 1165.
6 Phil. Mag., **20**, 539; **24**, 401.
7 Ann. chim. phys. [5], **29**, 198.

mercury and potassium were not equal to the sum of the thermal changes for the component salts, and concluded that the existence of double salts in such solutions was thereby proven.

Volume Changes.

Chemical changes being accompanied by volume change, the latter is often used as an index to the former. Kremers,[1] finding no change of volume on mixing solutions of salts capable of forming double salts, inferred that double salts are incapable of existence in water solution. A similar conclusion was drawn by Favre and Valson,[2] based on the fact that the density of a solution of potassium cupric sulphate is the mean of the densities of its constituents.

Gerlach,[3] however, noticed a slight contraction in volume on mixing solutions of the constituents of the alums. This became more marked as the concentration of the solutions increased. Upon this and other grounds he was led to the belief that these double salts exist as such in solutions. The conclusions of Groshans[4] from observations on double chlorides and sulphates confirmed those of Kremers.

Solubility of Salt Mixtures.

Researches upon the solubility of salt mixtures, especially upon the conditions of equilibrium in solution, when two salts capable of forming a double salt are dissolved together, have contributed to our knowledge of the existence of double salts in solution. From the work of Kopp[5] and others, extended by his own investigations, Mulder[6] drew the conclusion that well defined double salts exist in saturated solutions of salt mixtures. This conclusion was based upon the observation that in such solutions, saturated with respect to each component, the salts are often found in simple molecular proportions. Some work of Rüdorff[7] seemed to point to a different conclusion, but this has been interpreted otherwise by Trevor. The studies of equilibrium of Ditte[8] on the double iodide of lead and potassium ($PbI_2.K_2I_2.nH_2O$), of Rooze-

[1] Ann. der Phys. Pogg., **98**, 58.
[2] Compt. rend., **77**, 907.
[3] Ztschr. anal. Chem., **28**, 485.
[4] Des Dissolutions Aqueuses, 2–7.
[5] Ann. Chem. (Liebig), **34**, 260.
[6] Jsb. Chem., 1864, 92; 1866, 65.
[7] Ann. der Phys. Pogg., **148**, 558.
[8] Ann. chim. phys., [5], **24**, 226.

boom[1] on astrakanite, of Meyerhoffer,[2] Vriens,[3] Schreinemaker,[4] and van der Heide[5] have led to the general result that there are certain limits of temperature, outside of which double salts are capable of existing in their solutions.

From van't Hoff's application of the gas laws to solution, Nernst[6] deduced theoretically and quantitatively what had been already qualitatively established by experiment, that if to a saturated solution of a salt, a solution of another salt having a common ion, be added, the solubility of the first salt is decreased and a part of it precipitated. On examining certain cases in which the solubility of the first salt is increased under the conditions named above, Le Blanc and Noyes[7] succeeded in showing that the apparent exceptions were due to the formation of double salts in solution. Rose[8] attributed to the same cause those cases in which a salt is found to be more soluble in the solution of another salt than in water. The view that the solution of silver chloride in ammonia is accompanied by the formation of a double salt in the solution has been confirmed by Bodländer.[9]

Electrolysis.

The application of electrolysis to the study of the condition of double salts was made early in the present century by Parret,[10] who found that when potassium ferrocyanide was electrolyzed, alkali appeared at the negative pole while oxide of iron and prussic acid appeared at the positive. The work of Daniell and Miller[11] on the same salt, extended by Hittorf[12] to many other double salts, led to the view that double salts are of two classes; those which do not exist as such in solution, and those containing a metal combined with a complex radical, which are capable of existing in water solution, undecomposed. In the nomenclature which Ostwald[13] proposed the latter are called "complex salts;" the term "double salt" being applied to members of the first class only. To

1 Ztschr. phys. Chem., **2**, 513.
2 *Ibid*, **3**, 336.
3 *Ibid*, **7**, 194.
4 *Ibid*, **9**, 57.
5 *Ibid*, **12**, 416.
6 *Ibid*, **4**, 372.
7 *Ibid*, **6**, 385.
8 Ann. der. Phys. Pogg., **82**, 545.
9 Ztschr. phys. Chem., **9**, 730.
10 Phil. Trans. Lond., 1814, 527.
11 Ann. der Phys. Pogg., **64**, 18.
12 *Ibid*, **106**, 513.
13 Ztschr. phys. Chem., **3**, 596.

the complex salts he refers potassium ferrocyanide and analogous compounds. The alums are classed as double salts. Between these extreme types varying degrees of decomposition of the complex molecules may exist in solution.

Electrical Conductivity.

Researches upon the electrical conductivity of double salts and salt mixtures are numerous. Of chief importance in the present connection are those of Bouchotte[1] and Paalzow[2] on the sulphates of copper and zinc in common solution; of Svenson[3] on the alums, of Grotrian[4] on potassium cadmium iodide (K_2CdI_4) of Freund,[5] Bender,[6] Bouty,[7] Arrhenius,[8] and Chroustchoff and Packhoff[9], on mixtures of electrolytes; of Klein[10] on mixtures and double salts; of Wershoven[11] on dilute solutions of cadmium salts; and of Kistiakowsky[12] on dilute solutions of complex salts. The results of these investigations, in so far as they refer to the dissociation of double salts, agree in showing that with increasing dilution many double salts rapidly approach the condition of a simple mixture. Klein, who compared the conductivities of salt mixtures capable of forming double salts, with the conductivities of those whose constituents could not combine, showed that in the former case the difference between the conductivity of the mixture and the mean conductivity of its constituents was much greater than in the latter, for concentrated solutions. He inferred that in concentrated solutions of double salts there is only a partial breaking down of the complex molecules into their constituents. Kistiakowsky found that even in very dilute solutions of complex salts the complex ions remained undecomposed. The conductivity method has also been applied by Le Blanc and Noyes, by Bodländer, and others to the problem of the existence of double salts in solution, with the result that in certain cases the existence of such is indicated as probable.

1 Compt. rend., **62**, 955. 2 Ann. der Phys. Pogg., **136**, 489.
3 Ann. der Phys. Beibl, **2**, 46; Inaug. Dissertation, Lund.
4 Ann. der Phys. Wied, **18**, 177. 5 *Ibid*, **7**, 44.
6 *Ibid*, **22**, 179. 7 Ann. chim. phys. [6], **3**, 433; **14**, 74.
8 Ann. der Phys. Beibl, **9**, 437; Ann. der phys. Wied., **30**, 51.
9 Compt. rend., **108**, 1162. 10 Ann. der Phys. Wied., **27**, 151.
11 Ztschr. phys. Chem., **8**, 481. 12 *Ibid*, **6**, 97.

Lowering of the Freezing-point.

The application of the freezing-point method to the problem in question has been made, especially by Raoult.[1] By comparing the lowering caused by double salts with the sum of the lowerings of their constituents, he concluded that certain double sulphates, including the alums, are entirely decomposed into the simpler sulphates, when dissolved in water; while certain other double salts undergo only partial decomposition under the same conditions.

The foregoing summary of our knowledge with respect to the existence of double salts in solution, will show that the classification of such salts into two groups according as they are wholly or but partially decomposed by water, is well established so far as dilute solutions are concerned, but that in more concentrated solutions the evidence is not yet sufficient to regard the classification as satisfactory.

The present investigation was undertaken with the object of obtaining such further data as might justify more definite conclusions. The work thus far has been devoted mainly to the alums, as representatives of that extreme type of double salts which were supposed by some to be completely broken down in water solution. It has already been extended to one of the double chlorides, but since much more work will be necessary along this line before justifiable conclusions can be drawn, the results now in hand will be supplemented before they are published.

The conclusions reached in this paper with respect to the existence of the alums in solution, are based upon a comparison of the electrical conductivity and cryoscopic behavior of the double salts, with that of their constituent salts, with a view to determine to what extent the solutions of the double salts correspond to mixtures. Since the double sulphates correspond in general to one of the two types:

$$\text{I.}\quad R'_2SO_4 + R''SO_4 + 6H_2O.$$
$$\text{II.}\quad R'_2SO_4 + R'''_2(SO_4)_3 + 24H_2O,$$

any conclusions reached with respect to the alums in solution, would probably apply directly to a larger group of the double sulphates.

[1] Compt. rend., 99, 914.

The measurements of the conductivity of the solutions were made by the Kohlrausch method. The special form of the apparatus employed was that described by Ostwald.[1] The bridge wire was calibrated by the method of Strouhal and Barus.[2] Two resistance cells, with electrodes at different distances, were used—one for solutions more concentrated than 0.001 normal, the other for solutions more dilute. In this way satisfactory tone-minima were obtained throughout a wide range of dilution. The temperature selected for the measurements was in general 25°. By means of a thermostat the temperature was easily maintained constant to within one-tenth of a degree.

The flasks and pipettes used in making up the solutions were calibrated by the method of Morse and Blalock.[3] The solutions were standardized by the determination of some constituent, in a measured volume. In a few cases the nature of the salt allowed it to be weighed directly.

Since the conductivity of the water affects very considerably the conductivity of the more dilute solutions, all the water used was purified as follows: Ordinary distilled water was treated with potassium permanganate and a little sulphuric acid, and the vapor from this solution passed into distilled water containing permanganate and a little potassium or sodium hydroxide. The vapor from the second solution was condensed in a tube of block-tin. The apparatus used for purifying the water was found to be so efficient that it is sketched in some detail in Fig. I.

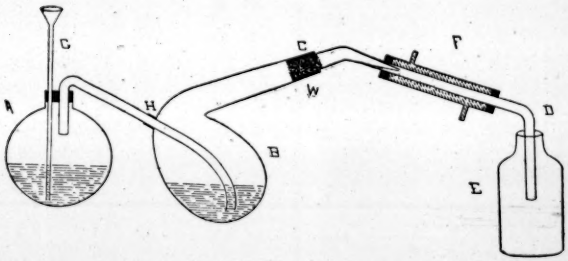
A is a balloon flask, preferably of Jena glass, holding from five to six liters. *B* is a tubulated retort of about four liters capacity. The two are connected by a glass tube of about 1 cm. diameter, bent as shown in the drawing. Where the tube enters the retort at *H* it is tightly wrapped with thin asbestos paper, forming a steam-tight joint. The use of a cork in contact with the steam in the retort is thus avoided. Into the neck of the retort, at *C*, is fitted an adapter, bent as shown in the drawing, and partly filled with glass wool, *W*. The joint is made secure by

[1] Ztschr. phys. Chem., **2**, 561. [2] Ann. der Phys. Wied., **10**, 326.
[3] This JOURNAL, **16**, 479

wrapping the end of the adapter with asbestos paper. The small end of the adapter projects well into the tin condenser *D*, which is surrounded by the cooling jacket *F*. *E* is a carefully cleaned flask, which receives the water from the condenser.

Ordinary distilled water is introduced into the vessel *A*, together with a little sulphuric acid and potassium permanganate, through the funnel tube *G*. It is heated to boiling, the vapor passing into *B*, which contains distilled water, potassium permanganate, and a little potassium or sodium hydroxide. A

FIG. 1



small flame is sufficient to keep the liquid in *B* at the boiling temperature. The vapor passes from *B* along the long neck of the retort, over the glass wool, which is meant to arrest any trace of permanganate carried along by the steam, into the tin condenser, and is received in the flask *E*. Certain precautions must be taken in fitting up and using the apparatus. The glass wool, *W*, introduced into the adapter arm, *C*, must fill only the lower part of the arm, otherwise there is danger that a trace of alkali will dissolve from it and be swept over into the condenser. The glass wool used should be washed well with dilute hydrochloric acid and heated for a long time in a current of water vapor. Whenever the apparatus is cleaned and refilled, which should be done about once a week when in constant use, the distillate collected at first must be discarded, since it always contains a trace of alkali, probably of

ammonia, formed by the action of the alkaline permanganate on the ordinary distilled water introduced into *B*. When this is once removed there is no further escape of ammonia possible, since the organic impurities in the water are destroyed by the permanganic acid in *A*, and the ammonia combines with the sulphuric acid present in that vessel. The carbon dioxide liberated in *A* is absorbed by the alkali in *B*. The process is thus perfectly continuous for at least a week, or it can be interrupted at any time by removing the burners. Four to five liters of water were obtained daily from this apparatus.

The water purified by this method gave a conductivity at 25° varying from 1.5 to 2×10^{-6} mercury units. The conductivity of the water used was measured for each series of determinations and the corresponding correction applied. In making a series of conductivity measurements, the general method adopted was to make up from the original solution, standardized by analysis, a solution which was a simple multiple or fraction of normal. Twenty-five or fifty cc. of this solution were then measured with a pipette into the cell and successive dilutions prepared from this in the cell itself, by withdrawal of a measured portion and addition of an equal volume of water. As a check upon errors of dilution, a series of solutions were made up directly in measuring flasks at intervals corresponding to several of the dilutions in the cell. These solutions were used as standards of conductivity, and when the conductivity of the cell dilution differed appreciably from the standard, a proportional correction was applied to the former, in the manner indicated by Kohlrausch.[1] When this correction exceeded one-half of 1 per cent. the measurements were repeated. The cell was standardized at frequent intervals with a one-fiftieth normal solution of potassium chloride, which had been recrystallized five times. In certain cases in which the solutions were found to be unstable at great dilutions, the check solutions were made up immediately before measuring their conductivity.

A Method for Titrating Aluminium.

The necessity of standardizing solutions containing alumin-

[1] Ann. der Phys. Wied., **26**, 184.

ium occurred so often in the progress of the work, that a reliable and convenient method of determining this element by titration was highly desirable. None of the methods described in the literature seem to have proved satisfactory. That of Baeyer[1], by the titration of sodium aluminate with sulphuric acid, using litmus and methyl orange as indicators, is described as a tedious and uncertain process, while in the method of Lunge[2] the ratio of the acid consumed to the aluminium has been the subject of much discussion.

After an unsuccessful attempt to titrate aluminum in the alum by means of a solution of barium hydroxide, the following method was devised. It gave, however, only fairly satisfactory results. A measured volume of the alum solution was heated nearly to boiling and all the sulphuric acid precipitated with barium chloride. Care should be taken to use only a small excess of the latter. A few drops of litmus were added and a one-twentieth normal solution of ammonia run in slowly and with constant shaking until the litmus showed a weakly alkaline reaction. A large excess of ammonia must be avoided, since it would dissolve to some extent the precipitated aluminium hydroxide. The change in the color of the litmus on adding the ammonia was gradual, and thus the aluminium could not be directly titrated with ammonia with any approach to accuracy, as we convinced ourselves by repeated trial. The solution containing the barium sulphate and aluminium hydroxide as precipitates, was diluted to a known volume and allowed to stand some hours until most of the precipitate had settled. It was found convenient to carry out the entire analysis in measuring flasks holding 100 cc. After the precipitate had settled a part of the solution was decanted and passed through a small filter paper, the first part of the filtrate being discarded to avoid change in the concentration of the ammonia by the filter paper. To 50 cc. of the filtrate a few drops of litmus were again added and the solution again titrated to color with standard hydrochloric acid. The second addition of the litmus is necessary, since the aluminium hydroxide acts as a mordant with the dye and removes almost completely that which was added at first.

[1] Ztschr. anal. Chem., **24**, 542; **25**, 183. [2] Ztschr. angew. Chem., **227**, 293.

A solution of potassium aluminium alum titrated by this method gave the following results:

Determinations.

I.	1 cc. solution	contains	0.0948	gram	alum.
II.	1 cc.	"	0.0946	"	"
III.	1 cc.	"	0.0945	"	"
IV.	1 cc.	"	0.0944	"	"
V.	1 cc.	"	0.0944	"	"
		Mean	0.0945	"	"

The result of the gravimetric analysis of this solution by precipitating the sulphuric acid with barium chloride gave 0.09486 gram alum in 1 cc.

The Conductivity Results.

The conclusions drawn from the conductivity results are based upon a comparison of the conductivity of the constituents of the alum, with the conductivity of the alum itself, under the same conditions, as has been stated. On examining the literature, we found that very few conductivity determinations of sufficiently concentrated solutions of the constituents of the alums had been made at 25°, and the temperature coefficients given were scarcely accurate enough for our purpose. Measurements of the conductivity of a number of solutions of potassium sulphate, aluminium sulphate, and chromium sulphate at 25° were therefore made.

Potassium Sulphate.

The salt, purified by repeated crystallization, was dried to constant weight in an air-bath, and solutions were prepared from a weighed amount of the dry salt.

In the following tables the conductivities are expressed as "molecular conductivities," as defined by Ostwald[1] instead of in "equivalent molecular" units, in order to facilitate the comparison of the conductivities of solutions containing equal numbers of gram-molecules per liter, but of different concentration if expressed as equivalent normal.

The symbols $\mu_v 15°$ and $\mu_v 25°$ denote respectively the molecular conductivities at 15° and 25°.

[1] Lehrb. d. allg. Chem., II, 621.

Table I.

K_2SO_4 [174.34.]

Gram-molecules per liter.	Volume.	$\mu_v 15°$.	$\mu_v 25°$.
0.333	3.0	....	157.4
0.250	4.0	134.7	167.9
0.2175	4.6052	....	170.2
0.10855	9.2104	....	186.9
0.1	10.0	148.2	187.0
0.05427	18.4208	....	202.8
0.5	20.0	162.9	205.1
0.0333	30.0	167.2	213.9
0.025	40.0	171.7	220.3
0.01666	60.0	179.4	229.1
0.005	200.0	200.7	252.4
0.0025	400.0	....	262.2
0.0005	2000.0	....	276.5
0.00025	4000.0	....	281.9
0.00005	20000.0	237.8	279.6

The only direct measurements of the conductivity of solutions of potassium sulphate, at 25°, available for comparison with our own, were those of Walden,[1] which, on interpolation gave values which agreed fairly well with our own, as can be seen by comparing Table II with Table I.

Table II.

Walden's Results for Potassium Sulphate.

Volume.	$\mu_v 25°$.
64	232.2
128	246.0
256	256.8
512	265.4
1024	272.8
2048	278.6

Aluminium Sulphate.

The so-called chemically pure aluminium sulphate was found to contain a large quantity of sodium which was difficult to remove, so that it was decided to prepare the salt from a pure aluminium compound. Perfectly pure potassium aluminium alum prepared by repeated crystallization was

[1] Ztschr. phys. Chem., **2**, 49.

treated with ammonia, which precipitated the aluminium as the hydroxide. The precipitate was then washed until it was found to be free from ammonia and potassium; this operation requiring several weeks. The washing was effected by boiling the precipitate with a large volume of water, for some time, allowing it to settle, and successively decanting and filtering. While the precipitate was on the filter, it was washed many times with boiling water. The hydroxide was then brought into a large beaker, treated with several liters of water and again boiled for a considerable time. This treatment was repeated from fifteen to twenty times, when a pure specimen of aluminium hydroxide was obtained. The pure hydroxide was dissolved in sulphuric acid, using a slight excess, as indicated by methyl orange, to prevent the formation of basic aluminium sulphates. The excess of acid was removed by dissolving the salt in water and precipitating it several times by adding alcohol.

The last traces of alcohol were removed by warming the salt gently in an air-bath. The aluminium sulphate thus obtained was a beautiful white powder. A qualitative analysis showed that it contained neither potassium nor ammonium. In a sample chosen, both the sulphuric acid and the aluminium were determined, with the result that they differed from the calculated equivalents well within the error of experiment. A solution of the salt was prepared, and standardized by determining the amount of sulphuric acid in a measured volume.

Determination.

I. $Al_2(SO_4)_3$ per cc. = 0.04470 gram.
II. " " " = 0.04478 "

Mean = 0.04474 "

The amount of the aluminium sulphate present in the solution was therefore equivalent to 0.1307 gram-molecules per liter.

In the following table of conductivity measurements of aluminium sulphate, it will be seen that two series, more or less complete, were carried out at 25°.

Table III.

$Al_2(SO_4)_3$ 342.34.

Gram-molecules per liter.	Volume.	μ_v15°.	I. μ_v25°.	II. μ_v25°.	Mean μ_v25°.
0.21715	4.6052	....	105.7	....	105.7
0.10855	9.210	107.7	130.3	....	130.3
0.06666	15.0	....	148.2	148.5	148.3
0.05427	18.4208	....	153.6	....	153.6
0.03333	30.0	139.1	172.5	172.7	172.6
0.016666	60.0	....	202.3	202.1	202.2
0.003333	300.0	243.6	300.4	300.8	300.6
0.001666	600.0	....	359.5	358.6	359.0
0.0005	1999.9	382.4	....	....	....
0.0003333	3000.0	....	530.0	531.7	530.8
0.00025	4000.0	447.4	....	....	....
0.0001666	6000.0	....	611.6	611.4	611.5
0.00003333	30000.0	....	806.1	809.1	807.6
0.000025	40000.0	678.4	....	....	....
0.0000166	60000.0	....	869.4	869.4	869.4
0.0000125	80000.0	708.7	....	....	....
0.00000625	160000.0	715.2	....	....	....

These results agree satisfactorily with some measurements of dilute solutions by Walden at the same temperature.

Chromium Sulphate.

The salt was prepared under the direction of Prof. Renouf of this laboratory, by reducing chromic acid with ether, under a bell jar, according to the method described in his "Inorganic Preparations," p. 78.

A very concentrated solution of the compound was made. In order to diminish the error of analysis, the solution standardized, was prepared from the original by diluting one volume to twenty.

Determination I. $Cr_2(SO_4)_3$ in 1 cc = 0.007426 gram.
" II. " " " " = 0.007410 "

Mean = 0.007418 "

Hence the original solution contained 0.3779 gram-molecules per liter.

The conductivity results for chromium sulphate are given in Table IV.

Table IV.

$Cr_2(SO_4)_3 = 392.58$.

Gram-molecules per liter.	Volume.	$\mu_v 15°$.	$\mu_v 25°$.
0.333	3	....	94.2
0.250	4	86.2	107.3
0.100	10	....	139.0
0.05	20	132.3	162.7
0.025	40	....	190.7
0.005	200	233.2	288.2
0.0025	400	....	346.5
0.0005	2000	....	558.2
0.00025	4000	....	671.2

The conductivity values found for chromium sulphate by Walden[1] differ widely from the above. A comparison of a few dilutions will show the extent of the difference. In Table V, column I, are Walden's values reduced to molecular conductivity units, column II our values, obtained by interpolation in the above results.

Table V.

Comparison of Results for Chromium Sulphate.

Volume.	I. $\mu_v 25°$.	II. $\mu_v 25°$.
192	378.0	283.4
384	439.2	342.0
1536	589.2	497.0
3072	669.6	617.0

The values of Walden are throughout much higher than our own. If the mean be taken of Walden's values for chromium sulphate and the values for the corresponding solutions of potassium sulphate, it would lead one to expect conductivity results for potassium chrome alum far larger than those found; since it is known that the conductivity of an alum is somewhere near the mean of the conductivity of its constituents. However, on account of this discrepancy, we propose to repeat the conductivity measurements with a new preparation of the chromium sulphate. Having determined the conductivity of these constituents of the alums, that of the alums themselves was next measured.

[1] Ztschr. phys. Chem., 1, 541.

Potassium Aluminium Alum.

The alum was purified by repeated crystallization and was found to be free from iron, sodium and ammonium, which might be present as impurities. The flame reaction was that of a clean potassium salt. A solution was prepared, approximately saturated at 20°, and was standardized by precipitating the sulphuric acid with barium chloride. The mean of three determinations gave $KAl(SO_4)_2 + 12H_2O$ in 1 cc. = 0.09486 grams, which is equivalent to 0.19995 gram-molecules per liter. The conductivity results are incorporated in Table VI.

Table VI.

$KAl(SO_4)_2 + 12H_2O = 474.41.$

Gram-molecules per liter.	Volume.	I. $\mu_v 25°$.	II. $\mu_v 25°$.	Mean of I and II.
0.19995	5.0012	133.9	133.9	133.9
0.125	8.0	149.2	149.2	149.2
0.05	20.0	178.3	178.3	178.3
0.025	40.0	202.5	202.5	202.5
0.005	200.0	268.2	269.9	269.0
0.0025	400.0	304.2	306.3	305.2
0.0005	2000.0	407.0	406.8	406.9
0.00025	4000.0	468.2	466.8	467.5

Sodium Aluminium Alum.

The alum was prepared by dissolving together equivalent quantities of sodium and aluminium sulphates so as to form a concentrated solution, placing this solution in a tall narrow glass cylinder and pouring on the water solution a thick layer of alcohol. This was allowed to stand for some time with the expectation that the alcohol would diffuse through the liquid below, causing the alum, which was very soluble in water, to crystallize out. This was found to require so much time that the process was hastened by jarring the cylinder occasionally. In the course of a few weeks, large crystals of sodium alum were formed, but with these were mixed a few crystals of some other salt, also soluble in alcohol with difficulty. When the mixture was treated quickly with a little cold water, the impurity readily dissolved, leaving the alum

crystals entirely free from any foreign matter, as could be verified under a microscope. The crystals were powdered and dried for a long time, to remove all traces of alcohol. A solution was prepared and standardized by gravimetric determinations of sulphuric acid.

Determination I, $NaAl(SO_4)_2 12H_2O$ in 1 cc. = 0.02402 gram
" II, " " 1 " = 0.02407 "

Mean = 0.02404 "

The conductivity results are given in Table VII.

Table VII.

$NaAl(SO_4)_2 + 12H_2O = 458.33$.

Gram-molecules per liter.	Volume.	I. $\mu_v 25°$.	II. $\mu_v 25°$.	Mean.
0.05	20.0	161.5	161.6	161.6
0.025	40.0	184.4	184.7	184.6
0.005	200.0	250.0	251.2	250.6
0.0025	400.0	286.7	284.2	285.4
0.0005	2000.0	380.0	378.8	379.5
0.00025	4000.0	435.5	435.2	435.4

Ammonium Aluminium Alum.

The salt, after eleven crystallizations, was found to be free from sodium, but still contained a trace of potassium. A solution was standardized by titrating the aluminium.

Determination.

I. $NH_4Al(SO_4)_2 + 12H_2O$ in 1 cc. = 0.04550 gram.
II. " " 1 " = 0.04585 "

Mean = 0.045675 "

The solution contained therefore 0.10076 gram-molecules. The conductivity results are given in table VIII.

Table VIII.

$NH_4Al(SO_4)_2 + 12H_2O = 458.33$.

Gram-molecules per liter.	Volume.	I. $\mu_v 25°$.	II. $\mu_v 25°$.	Mean.
0.1	10.0	152.8	152.9	152.8
0.05	20.0	174.5	175.0	174.8
0.025	40.0	198.1	198.4	198.2
0.005	200.0	261.4	260.6	261.0
0.0025	400.0	297.1	294.9	296.0
0.0005	2000.0	390.0	389.2	389.6
0.00025	4000.0	452.4	452.4	452.4
0.00005	20000.0	568.4	560.0	564.2
0.000025	40000.0	608.4	602.8	605.6

Potassium Chrome Alum.

The salt, purified by repeated crystallization from water at 35°, was dissolved, and the solution standardized by precipitating the sulphuric acid as barium sulphate.

The analysis gave :

I. 0.11742 gram $KCr(SO_4)_2 + 12H_2O$ per cc.
II. 0.11846 " " " "

Mean 0.11744 gram chrome alum per cc. This is equivalent to 0.2351 gram-molecules per liter.

In the following table are incorporated the results of the measurements of conductivity of the solutions :

Table IX.

$KCr(SO_4)_2 + 12H_2O = 499.53$.

Gram-molecules per liter.	Volume.	I. $\mu_v 25°$.	II. $\mu_v 25°$.	Mean.
0.1	10.0	147.8	148.1	147.9
0.05	20.0	170.5	170.3	170.4
0.025	40.0	195.4	195.0	195.2
0.005	200.0	266.7	266.5	266.6
0.0025	400.0	306.1	304.9	305.5
0.0005	2000.0	418.6	418.8	418.7
0.00025	4000.0	472.4	471.6	472.0

Ammonium Chrome Alum.

The salt was purified as in the case of potassium chrome

alum, the solution prepared and standardized in the same manner. The result of the analysis was:

I. 1 cc. of solution contained 0.09266 gram $NH_4Cr(SO_4)_2 + 12H_2O$.

II. 1 cc. of solution contained 0.09282 gram $NH_4Cr(SO_4)_2 + 12H_2O$.

Mean = 0.09274 gram, which corresponded to 0.194 gram-molecules per liter. The conductivity results are given in Table X.

Table X.

$NH_4Cr(SO_4)_2 + 12H_2O = 478.44$.

Gram-molecules per liter.	Volume.	I. $\mu_v 25°$.	II. $\mu_v 25°$.	Mean.
0.1	10.0	145.4	144.7	145.0
0.05	20.0	167.2	167.1	167.1
0.025	40.0	191.5	191.1	191.3
0.005	200.0	263.8	263.6	263.7
0.0025	400.0	304.0	303.6	303.8
0.0005	2000.0	....	415.3	415.3
0.00025	4000.0	484.6	477.5	481.0

As is well known, solutions of chromium salts become green at a temperature between 70° and 80°. In this latter state they cease to have the power to deposit crystals. Recoura[1] has shown that the green modification is a well defined basic salt mixed with free acid, and Monti[2] has found that the change in color is accompanied by a rise in the conductivity. The recent work of Whitney,[3] using two widely different methods, confirms Recoura in his conclusion that the green modification is a basic salt and that free sulphuric acid is present in the solution. In order to determine whether the passage over into the green modification is discontinuous at any point, a series of experiments was made by placing the conductivity cell, containing a solution of ammonium chrome alum, in a bath, and regularly increasing the temperature with the time. Noting the temperature, the conductivity measurements were made at more or less regular time intervals.

[1] Ann. chim. phys., [7], 4, 494. [2] Ztschr. anorg. Chem., 12, 75.
[3] Ztschr. phys. Chem., 20, 40.

The following results can be regarded as relatively correct, but on account of the difficulty in measuring the temperature these values are probably each a little too low. In the following table are the conductivity results for a one-twentieth gram-molecular normal solution of ammonium chrome alum, for temperatures from 37°.5 to 90°.

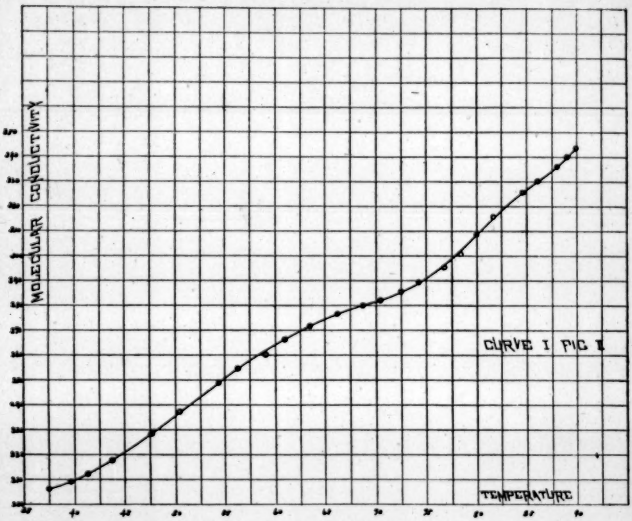
Table XI.

Temperature.	Time. Minutes.	μ_v.
37°.5	..	207.0
39°.5	6	209.8
41°.4	8	213.6
43°.5	10	218.8
47°.5	13	229.2
50°.4	15	236.4
52°.5	17	243.0
54°.5	19	248.4
56°.5	20	254.4
59°.0	22	260.6
61°.0	24	266.0
63°.5	25	271.4
66°.4	28	277.0
68°.4	30	280.2
70°.4	32	283.0
72°.4	33	286.6
74°.3	..	290.0
76°.7	38	295.2
78°.4	40	301.2
80°.2	42	309.4
81°.8	..	316.8
83°.4	45	321.8
84°.7	..	325.8
86°.2	48	330.4
88°.0	..	336.4
89°.2	..	340.6
90°.0	53	343.4

These results are plotted in Curve 1, Fig. II, from which it will be seen that the transformation to the green modification is continuous as the temperature rises.

Ammonium Iron Alum.

A solution of the recrystallized salt was standardized by re-



ducing the ferric to ferrous iron, and reoxidizing the iron by means of standard potassium permanganate. The results of analysis were:

I. 0.24772 gram of $NH_4Fe(SO_4)_2 + 12H_2O$ in 1 cc.
II. 0.24722 " " " " 1 "
Mean 0.24747 " " " " 1 "

The solution was therefore 0.5089 gram-molecular normal. Table XII gives the results of the measurements of the conductivity.

Table XII.

$NH_4Fe(SO_4)_2 + 12H_2O = 482.24.$

Gram-molecules per liter.	Volume.	$\mu_v 25°$.
0.25	4.0	118.9
0.05	20.0	177.4
0.025	40.0	211.5
0.005	200.0	320.2

Instability of Some Alums in Dilute Solution.

In the course of the measurements of the conductivity of dilute solutions of some of the alums, it was observed that the conductivity increased at a more or less rapid rate on standing for a time. As such a change in conductivity must depend upon some change in the condition of the dissolved substance, this observation would indicate that some alums are unstable in the presence of a large volume of water, and, as will be seen, the alums possess different degrees of stability. In table XIII are given the dilutions at which the changes in the conductivity μ_v, with the time which elapsed, were studied.

Table XIII.

Sodium Aluminium Alum.

Volume.	μ_v.	Time.
20000	529.6	0 hours.
"	550.0	24 "

Ammonium Chrome Alum.

Volume.	μ_v.	Time.
20000	630.0	0 hours.
"	686.0	24 "

Ammonium Iron Alum.

Volume.	μ_v.	Time.
200	320.2	.0 hours.
"	330.0	2 "
400	411.0	0 "
"	424.0	20 minutes.
2000	694.0	0 "
"	808.8	30 "
"	891.0	18 hours.
"	896.0	21 "

An increase in the conductivity with the time was noticed in the case of the sodium aluminium and ammonium chrome alums, but not until a dilution of approximately 20,000 liters was reached. The former showed an increase of about four per cent. in twenty-four hours. But a much more marked example of instability was brought out in a study of the ammonium iron alum, as is seen in the above table. At a dilution of 200 liters, the conductivity rose three per cent. in two hours. At

400 liters, it showed the same increase in twenty minutes, while at a dilution of 2000 liters, the rate of increase was at first about one and one-half per cent. per minute. This rate quickly diminished with time, and at the end of twenty-four hours an apparent state of equilibrium was reached, with a total increase in the conductivity of about thirty per cent. When the experiment was conducted at 0°, a dilution of 1000 liters was reached before decomposition began. The precipitate formed in the decomposition of the ferric ammonium alum did not appear until after the change in conductivity was observed.

Examples of the rise in the conductivity of dilute solutions have been observed by Kohlrausch[1] in the case of barium nitrate, copper sulphate, and other salts. For the first compound, this was clearly caused by the formation of a basic salt, and the liberation of free acid. The ease with which chromium forms basic salts with rise in temperature has already been considered. The well known tendency of iron ammonium alum to form basic salts is doubtless the cause of the rise in the conductivity of this substance, due to the action of a large volume of water. It seems probable, therefore, that a similar change occurs in very dilute solutions of sodium aluminium and ammonium chrome alums. Such a change would be analogous to that studied by Rose[2] in the case of acid potassium sulphate, which is decomposed by a large volume of water, forming the neutral sulphate and free acid.

Comparison of Conductivity Results.

If the conductivities of the alums are compared, it will be seen that throughout all dilutions, these bear the same relation to one another as the conductivities of their constituents. The conductivities of potassium, sodium and ammonium sulphates stand in the same order as the conductivities of the corresponding alums. A detailed comparison of the conductivities of the alums with the arithmetical mean of the conductivities of their constituents, is given in the tables which follow. The data for the values of the conductivity of

[1] Ann. der Phys. Wied., **26**, 175. [2] Ann. der Phys. Pogg., **82**, 545.

aluminium sulphate have been taken from our own results for that compound, supplemented by those of Walden,[1] by interpolation by the graphic method. The data for sodium sulphate are interpolated values from Kohlrausch's[2] tables, reduced to 25° and changed to molecular conductivity units. The values for potassium sulphate and chromium sulphate are taken directly from the tables already given. No data for ammonium sulphate and ferric sulphate are at present available. Since the latter exists only in acid solution, direct observations of its conductivity would have no value for the present purpose.

Table XIV.

Potassium Aluminium Alum.

Volume.	K_2SO_4 $\mu_v 25°$.	$Al_2(SO_4)_3$ $\mu_v 25°$.	Arithmetic mean.	Alum observed. $\mu_v 25°$.	Difference, per cent.
5.0012	172.7	108.0	140.3	133.9	—4.5
8.0	183.3	124.2	153.7	149.2	—3.0
20.0	205.1	158.1	181.6	178.3	—1.7
40.0	220.3	185.7	203.0	202.5	—0.2
200.0	252.4	290.4	271.4	269.0	—0.8
400.0	262.2	342.6	302.4	305.2	+0.9

Table XV.

Sodium Aluminium Alum.

Volume.	Na_2SO_4 $\mu_v 25°$.	$Al_2(SO_4)_3$ $\mu_v 25°$.	Arithmetic mean.	Alum observed. $\mu_v 25°$.	Difference. Per cent.
20.0	171.5	158.1	164.8	161.6	—1.9
40.0	183.1	185.7	184.4	184.6	+0.1
200.0	211.6	290.4	251.0	250.6	—0.2
400.0	219.1	342.6	280.8	285.4	+1.6

Table XVI.

Potassium Chrome Alum.

Volume.	K_2SO_4 μ 25°.	$Cr_2(SO_4)_3$ $\mu_v 25°$.	Arithmetic mean.	Alum observed. $\mu_v 25°$.	Difference. Per cent.
10.0	187.0	139.0	163.0	147.9	—9.2
20.0	205.1	162.7	183.9	170.4	—7.3
40.0	220.3	190.7	205.5	195.2	—5.0
200.0	252.4	288.2	270.3	266.6	—1.3
400.0	262.2	346.5	304.3	305.5	+0.4
2000.0	276.5	558.2	417.3	418.7	+0.3
4000.0	281.9	671.2	476.5	472.0	—0.9

[1] Ztschr. phys. Chem., 1, 541. [2] Ann. der Phys. Wied., 26, 196.

A study of the preceding tables seems to justify the following statements: First, in concentrated solutions the conductivity of the alums is notably less than the mean of the conductivities of their constituents; second, the "difference" is very nearly the same for the aluminium alums, while it becomes much greater for the chrome alum; third, the difference grows rapidly less with increasing dilution, so that at 40 liters for alnminium alums, and at about 400 for the chrome alum, it has practically disappeared.

Deductions from these facts must depend upon the relations which exist between the conductivity of a mixture of two electrolytes having a common ion, and the conductivities of the constituents taken separately. It has been shown, especially by the work of Bender and Klein, that in such mixtures the conductivity is in general less than the mean of the conductivities of the constituent salts. But Klein showed that the difference was much greater, when the salts were capable of forming a double salt. Thus, while potassium sulphate and sodium sulphate gave a difference of one per cent., potassium sulphate with ferrous sulphate gave a difference of six per cent. The "difference" found for the more concentrated solutions of the alums, is of the same order of magnitude ($2\frac{1}{2}$ to 11 per cent.), as that found by Klein for the double salts which he studied.

The condition that two electrolytes, having a common ion, may mix without undergoing a change in ionization, has been deduced from the dissociation theory of electrolytic conduction by Arrhenius.[1] If no change in volume occurs on mixing, that condition is that the concentration of the ions, *i. e.*, the quotient of the coefficient of ionization divided by the volume containing one gram-molecule, shall be the same for both solutions, or

$$\frac{\alpha_1 n_1 v_1}{v_1} = \frac{\alpha_2 n_2 v_2}{v_2},$$

where α_1, α_2 are the coefficients of ionization of the respective solutions; n_1, n_2 the number of gram-molecules contained respectively in a unit of volume of each; and v_1, v_2, the respec-

[1] Ztschr. phys. Chem., 2, 284.

tive volumes of the solutions mixed. The following table shows the extent to which this condition is fulfilled in some of the solutions of alums which we employed. On the assumption that we may regard a solution of an alum as having been formed by mixing equal volumes of solutions of its constituents of the same molecular concentration, n_1 and n_2 in the preceding equation become equal, as also v_1 and v_2, and it is necessary only to compare the values of α_1 and α_2 for the constituent solutions.

The values of α have been calculated from freezing-point data instead of from conductivity, since the experimental error in measuring μ_∞ for aluminium sulphate may become very large. For potassium sulphate, the two methods yield concordant results, as is shown in the table given by Arrhenius.[1] In calculating the values of i, the ratio between the observed and the normal osmotic pressure, the value 1.88 was taken as the normal molecular lowering. The corresponding values of α are calculated from the equation

$$i = 1 + (K - 1)\,\alpha,$$

in which K denotes the number of ions into which each molecule dissociates; *three* for potassium sulphate and *five* for aluminium sulphate.

Table XVII.

Gram-molecules per liter.	K_2SO_4.		$Al_2(SO_4)_3$.		$Cr_2(SO_4)_3$.	
	i.	α.	i.	α.	i.	α.
0.117	2.22	0.61	...	...	2.20	0.30
0.1086	2.28	0.64	2.13	0.28	...	...
0.10	2.30	0.65	...	...	2.21	0.30
0.098	...	...	2.21	0.30	...	...
0.088	2.33	0.66	...	...	2.28	0.32
0.0653	...	...	2.34	0.33	...	...
0.059	2.41	0.70	...	...	2.40	0.35
0.054	2.45	0.72	...	...	...	...
0.05	2.44	0.72	2.44	0.38	2.44	0.38
0.0333	2.57	0.78	...	...	...	...
0.0294	2.57	0.78	...	...	2.55	0.387
0.026	...	...	2.60	0.40	...	...

It is thus apparent that the values of α, and therefore of

[1] Ztschr. phys. Chem., 2, 491.

$\frac{\alpha}{v}$, or the concentration of the ions of potassium sulphate, differs widely from that for either aluminium or chromium sulphate, while for the last two the values of α show an almost complete agreement throughout the range of dilutions given. The change in the dissociation produced by mixing either chromium or aluminium sulphate with potassium sulphate, whatever it may be, should therefore be nearly the same in both cases, if we neglect the effect of changes in volume, which in these cases is extremely small. Reference to the preceding tables shows that the difference is by no means the same for the aluminium and chromium alums; the "difference" being four or five times greater in the case of the chromium alum at the same dilution. It is also much greater, if we compare the solution at equal distances from the point of saturation. If we, therefore, even conclude that the potassium aluminium alum were entirely decomposed in concentrated solution, (which is probably not true), we must still admit that the molecules of the double salt in a concentrated solution of chromium alum are only partially broken down. This conclusion with reference to chromium alum agrees with that reached on other grounds by Carey Lea,[1] who, by the use of a reagent for the detection of free sulphuric acid in the presence of sulphates, finds that chrome alum is the only one present as such in solution.

In order to determine whether the solution of an alum is simply equivalent to a mixture of solutions of its constituents, a number of mixtures of equal volumes of solutions of potassium sulphate and aluminium sulphate of the same molecular concentration were prepared, and also of potassium sulphate and chromium sulphate. The conductivities of the constituent salts were observed, then that of the mixture. The results are given in Tables XVIII and XIX.

[1] Ztschr. anorg. Chem., 4, 445.

Table XVIII.

Potassium Sulphate and Aluminium Sulphate.

Gram-molecules per liter.	K_2SO_4 $\mu_v 25°$.	$Al_2(SO_4)_3$ $\mu_v 25°$.	Mean.	Mixture observed $\mu_v 25°$.	Difference, per cent.
0.2175	170.2	105.7	137.9	129.1	—6.4
0.10855	186.9	130.3	158.6	151.8	—4.3
0.05427	202.8	153.6	178.2	174.2	—2.2
0.03333	213.9	172.5	193.1	190.1	—1.6
0.01666	229.1	202.2	215.6	214.3	—0.6

Table XIX.

Potassium Sulphate and Chromium Sulphate.

Gram-molecules per liter.	K_2SO_4 $\mu_v 25°$.	$Cr_2(SO_4)_3$ $\mu_v 25°$.	Mean.	Mixture observed $\mu_v 25°$.	Difference, per cent.
0.333	157.4	94.2	125.8	113.0	—10.1
0.250	167.9	107.3	137.6	125.1	—9.0
0.100	187.0	139.0	163.0	155.1	—4.9
0.05	205.1	162.7	183.9	177.9	—3.3
0.025	220.3	190.7	205.5	202.8	—1.3

The conductivity of the mixture is thus always less than the mean of the conductivities of the constituent sulphates, the "difference" being greater the more concentrated the solutions. This is the same fact which was observed in the case of the alums, whose conductivity was less than the mean of their constituents.

On comparing the conductivities of the mixtures with those of the alums at the same concentrations, a close agreement is observed in the case of potassium aluminium alum, showing that we may regard a solution of this alum as having been formed by mixing equal volumes of solutions of its constituents of the same molecular concentration. A striking fact is brought out by comparing the conductivity of potassium chrome alum with that of the "mixtures" of the same concentration, the conductivity of the alum being less than that of the mixtures. It must be observed that volume changes play an unimportant part in this connection, since, according to Gerlach[1] the contraction at 15°, for a mixture of potassium and aluminium sulphates containing 0.21 gram-molecule per

[1] Ztschr. anal. Chem., **28**, 505.

liter, is 0.06 per cent., and for a mixture of potassium and chromium sulphates, containing 0.27 gram-molecule per liter, is at the same temperature, 0.12 per cent. If the difference noticed is well founded, it might be accounted for by supposing that the molecules of the double salt remain, in part, undecomposed and therefore not completely dissociated into the simplest ions, when its crystals are dissolved, but that the molecules of the constituent salts do not necessarily unite when their solutions are mixed. This is the explanation offered by Graham[1] of the fact observed by him, that the diffusion of the double sulphates of potassium and magnesium differed from that of a mixture of its constituent salts. The conclusions drawn in reference to potassium chrome alum, based on isohydric considerations, cannot perhaps be regarded as absolutely proven from the conductivity measurements alone, but must be regarded as highly probable.

Summary of Conductivity Results.

The preceding results, in so far as they bear upon the existence of the alums as such in solution, may be summarized as follows:

1. The alums, in dilute solution, have a conductivity which is almost exactly the mean of the conductivities of their constituents, from which it follows that the complex alum molecules are broken down completely in such solutions, into the molecules of the simpler sulphates, and that these simpler molecules dissociate as if alone, barring the effect on the dissociation produced when the solutions are not isohydric.

2. In concentrated solutions the alums show a conductivity less than the mean of the conductivities of their constituents. The difference becomes more marked as the concentration increases and is of the same order as that observed for other double sulphates. It is much greater than that found in the case of mixtures of sulphates incapable of yielding a double salt. This must be regarded as evidence that the alums are partially undecomposed into the constituent molecules in such solutions, or that the dissociation into the simple ions into which the single sulphates break down is not complete.

[1] Phil. Trans. Lond., 1850, 1.

3. The magnitude of the "difference" for potassium chromium alum, as compared with the aluminium alums, affords strong evidence that this alum at least, exists as such in moderately concentrated solutions.

Freezing-Point Measurements.

The apparatus used in the freezing-point determinations was of the ordinary Beckmann form, the inner tube containing the solution being considerably larger than in the ordinary apparatus, to prevent the possibility of touching the bulb of the thermometer with the stirrer. This tube contained no side tube. The solutions used were made up from the same standardized solutions as were employed in the conductivity work. The freezing-point was determined as quickly as possible after the solutions were prepared. In every determination, the zero of the water used in making up that solution, was taken.

The following tables contain the freezing-point lowerings obtained for the alums and their constituent salts.

G denotes the number of grams of the salt in a liter of solution; N the number of gram-molecules per liter. L denotes the corrected lowering of the freezing-point, corrected for the change in concentration of the solution due to the separation of ice, according to the formula deduced by one of us:

$$T = \frac{su'}{w}$$

in which T is the fraction of the liquid which solidifies, s the specific heat of the liquid, u the amount of undercooling in degrees Celsius, and w the heat of solidification of a unit weight of the liquid. Δ denotes the gram-molecular lowering of the freezing-point.

In the case of the alums the double formulas are used in expressing the freezing-point lowerings, for convenience in comparison with the lowerings of their constituents, the sum of the lowerings for the constituents being then directly comparable with the lowerings of the alums themselves.

[1] Jones, Phil. Mag., 36, 468.

Table XX.

$K_2SO_4 = 174.34$, 1st Series.

No.	G.	N.	L.	Δ.
1	37.857	0.217	0.890°	4.10
2	18.9285	0.1086	0.466	4.29
3	9.4643	0.0543	0.250	4.61
4	5.8110	0.0333	0.161	4.83
5	2.9055	0.0167	0.084	5.03

Table XXI.

$K_2SO_4 = (174.34)$, 2nd Series.

No.	G.	N.	L.	Δ.
1	58.1134	0.333	1.311°	3.93
2	43.5850	0.250	1.004	4.02
3	17.434	0.100	0.432	4.32
4	8.717	0.050	0.230	4.60
5	4.3585	0.025	0.122	4.88

Table XXII.

$Al_2(SO_4)_3 = (342.34)$, 1st Series.

No.	G.	N.	L.	Δ.
1	44.740	0.131	0.516°	3.94
2	33.555	0.098	0.410	4.18
3	22.370	0.0653	0.288	4.41
4	15.659	0.0457	0.212	4.64
5	8.948	0.0261	0.127	4.87
6	6.711	0.0196	0.101	5.15
7	4.474	0.0131	0.073	5.57

Table XXIII.

$Al_2(SO_4)_3 = 342.34$. 2nd Series.

No.	G.	N.	L.	Δ.
1	74.338	0.217	0.832°	3.83
2	37.169	0.1086	0.438	4.03
3	18.5845	0.0543	0.245	4.51
4	11.411	0.0333	0.189	4.77
5	5.7055	0.0166	0.088	5.30

Table XXIV.

$Cr_2(SO_4)_3 = 392.58$.

No.	G.	N.	L.	Δ.
			Salt probably	
1	130.860	0.333	separated on freezing.	
2	98.145	0.250	1.029°	4.12
3	39.258	0.100	0.417	4.17
4	19.629	0.05	0.230	4.60
5	9.8145	0.025	0.121	4.84

Table XXV.

$(NH_4)_2SO_4 = 132.16$.

No.	G.	N.	L.	Δ.
1	26.432	0.2	0.829°	4.145
2	13.216	0.1	0.437	4.370
3	9.2512	0.07	0.316	4.514
4	6.608	0.05	0.237	4.740
5	3.9648	0.03	0.148	4.933
6	1.9824	0.015	0.075	5.00

Table XXVI.

$K_2Al_2(SO_4)_4 + 24H_2O = 948.82$.

No.	G.	N.	L.	Δ.
1	47.441	0.05	0.409°	8.18
2	35.5807	0.0375	0.320	8.53
3	23.720	0.025	0.222	8.88
4	11.8575	0.0125	0.120	9.60
5	4.7430	0.005	0.057	11.40

Table XXVII.

$Na_2Al_2(SO_4)_4 + 24H_2O = 916.66$.

No.	G.	N.	L.	Δ.
1	22.9165	0.025	0.229°	9.16
2	11.4582	0.0125	0.125	10.00
3	5.7291	0.00625	0.009	11.04

Table XXVIII.

$(NH_4)_2Al_2(SO_4)_4 + 24H_2O = 906.6$.

No.	G.	N.	L.	Δ.
1	45.330	0.05	0.408°	8.16
2	33.997	0.0375	0.318	8.48
3	22.665	0.025	0.224	8.96
4	11.332	0.0125	0.121	9.68
5	5.666	0.00625	0.066	10.56

Table XXIX.

$K_2Cr_2(SO_4)_4 + 24H_2O = 999.0.$

No.	G.	N.	L.	Δ.
1	117.44	0.117	0.888°	7.59
2	88.08	0.088	0.686	7.80
3	58.72	0.059	0.480	8.14
4	29.36	0.0294	0.267	9.08
5	17.618	0.0176	0.170	9.66
6	11.744	0.0117	0.119	10.17
7	5.872	0.0059	0.065	11.02

Table XXX.

$(NH_4)_2Cr_2(SO_4)_4 + 24H_2O = 956.8.$

No.	G.	N.	L.	Δ.
1	92.740	0.097	0.768°	7.92
2	46.370	0.0484	0.400	8.26
3	27.822	0.0291	0.266	9.14
4	16.6932	0.0174	0.168	9.65
5	11.1288	0.0116	0.117	10.09
6	5.5644	0.0058	0.064	11.04

Table XXXI.

$(NH_4)_2Fe_2(SO_4)_4 + 24H_2O = 964.42.$

No.	G.	N.	L.	Δ.
1	247.72	0.257	1.820°	7.08
2	185.79	0.192	1.400	7.29
3	123.86	0.128	0.927	7.24
4	92.895	0.096	0.713	7.43
5	61.930	0.064	0.505	7.89
6	37.158	0.0385	0.322	8.36
7	24.772	0.0257	0.227	8.83
8	12.386	0.0128	0.121	9.45
9	6.193	0.0014	0.066	10.31

Comparison of Freezing-Point Results.

Comparing the results for the different alums, as shown in the foregoing tables, it is seen that as regards the aluminium alums, the sodium alum (Table XXVII) gives a somewhat greater depression, for corresponding dilutions, than either the potassium (Table XXVI) or the ammonium (Table XXVIII) alum. The lowerings given by potassium alum correspond closely to, but are slightly greater in con-

centrated solutions than those of the ammonium alum. In the more dilute solutions the reverse is true, but since the experimental error is here much larger, less value is to be attached to the results. The ammonium chrome and potassium chrome alums show closely agreeing values for corresponding dilutions (Tables XXIX and XXX), while these values are somewhat greater for the same dilutions than those of the aluminium alums.

In the following tables a comparison of the lowerings produced by the alums themselves with the sum of the lowerings of their constituents at the same dilution is given. The values for the constituent salts are interpolated from Tables XX to XXV.

Table XXXII.

Potassium Aluminium Alum.

N.	K_2SO_4 Δ.	$Al_2(SO_4)_3$ Δ.	Sum.	K-Al-alum. Δ.	Difference.
0.05	4.61	4.60	9.21	8.18	1.03
0.0375	4.76	4.72	9.48	8.53	0.95
0.025	4.89	4.91	9.80	8.88	0.92
0.0125	5.02	5.61	10.63	9.60	1.03

Table XXXIII.

Ammonium Aluminium Alum.

N.	$(NH_4)_2SO_4$ Δ.	$Al_2(SO_4)_3$ Δ.	Sum.	Amm-Al.-alum Δ.	Difference.
0.05	4.74	4.55	9.29	8.16	1.13
0.0375	4.86	4.72	9.58	8.48	1.10
0.025	4.95	4.01	9.86	8.96	0.90
0.0125	5.02	5.61	10.63	9.68	0.95

Table XXXIV.

Potassium Chrome Alum.

N.	K_2SO_4 Δ.	$Cr_2(SO_4)_3$ Δ.	Sum.	K-Cr-Alum Δ.	Difference.
0.117	4.28	4.16	8.44	7.59	0.85
0.088	4.38	4.27	8.65	7.80	0.85
0.059	4.54	4.51	9.05	8.14	0.91
0.0294	4.83	4.80	9.63	9.08	0.55

Table XXXV.

Ammonium Chrome Alum.

	$(NH_4)_2SO_4$	$Cr_2(SO_4)_3$	Amm-Cr-alum.		
N.	Δ.	Δ.	Sum.	Observed.	Difference.
0.097	4.38	4.19	8.57	7.92	0.65
0.0484	4.76	4.61	9.37	8.26	1.11
0.0291	4.93	4.81	9.74	9.14	0.60

The results here tabulated show that the lowerings produced by the alums, in the more concentrated solutions, are uniformly 10 to 11 per cent. less than the sum of the lowerings of their constituents, ammonium chrome alum excepted. Here the difference is considerably smaller, being only about 7.3 per cent. This is probably due to some experimental error, since other values obtained for this compound are in agreement with those for the other alums.

Raoult[1] found a lowering for potassium aluminium alum, which was only 1.2 of a per cent. less than the sum of the lowerings of the constituents. He inferred that the decomposition of the alum molecules in solution was complete. He does not, however, state the concentration which he employed and that is of course of importance in this connection.

The freezing-point determinations which we have carried out must be regarded as confirming the evidence from conductivity, that the alum molecules exist to some extent in the more concentrated solutions.

SILICIDES OF COPPER AND IRON.

By G. de Chalmot.

Copper Silicide.—In a former article[2] I described a crystalline silicide of copper having probably the composition Cu_3Si_2. At the time I had not much more of this material than was necessary for analysis, and lack of time prevented me from carrying the investigation further. At about the same time Vigoureux[3] published an article in which he described the compound Cu_3Si, and wherein he makes it appear unlikely that any other copper silicide containing more silicon than Cu_3Si exists.

1 Compt. rend., 99, 914. 2 This Journal, 18, 95.
3 Compt. Rend., 122, 318.

I have now investigated this matter again, and I have found that the crystals which I described are in fact no chemical compound, but a mixture of silicon, copper silicide, and copper.

I found at the time that *aqua regia* decomposes only a part of the crystals, but examining the undissolved residue, I found it to contain copper. I have now, however, succeeded in extracting all the copper from this residue, in case the material was very finely pulverized and heated for a considerable time with the acid mixture, and I have shown that the residue contained crystalline silicon. There is another reason why I did not give due attention to the fact that *aqua regia* attacks only a part of the crystals. I found that it does not completely decompose copper-silicon alloys containing only 13 to 14 per cent. of silicon. In regard to this subject I shall have more to say presently.

It is a remarkable coincidence, that in several instances I have found the composition of these crystals to be about that represented by the formula Cu_3Si_2. In other cases, however, they contain much more silicon, and especially when they appear to be purer. This led me to the belief that absolutely pure crystals would prove to consist only of silicon, but a small sample which was very carefully selected, with the aid of a strong glass, contained only 55.67 per cent. of silicon. I also picked out under the microscope several small apparently quite pure crystals, and treated them with cold *aqua regia*. They invariably broke up into many small pieces, and a considerable amount of copper was dissolved. Several of the small silicon crystals, which result from this treatment, retain the same brilliancy as the crystals of which they formed a part. The most perfect crystals are found in cavities in the interior of the pieces of copper silicide, that are formed in the furnace. These crystals are very flat, and of great brilliancy. They have very sharp edges and corners.

Vigoureux called attention to the fact that the copper-silicon alloys tarnish easily and become reddish. The crystals in question also tarnish, but only in spots or lines, most places remaining brilliant bluish-white. They sometimes as-

sume an appearance as if they were cracked all over. The outer surface, therefore, may mainly be formed by silicon crystals. I have found similar crystalline formations in alloys of manganese and iron with silicon. In the case of manganese I have shown them to contain crystalline silicon, and the compound $MnSi_3$.

In order to find out whether the copper in the crystals was present in the form of the compound Cu_2Si, or as a silicide containing more silicon, I determined the composition of several samples and also the amount of free silicon which they contained. For determining the latter, I pulverized the material and sifted it through fine linen. I then heated it for 6 to 8 hours with *aqua regia* and, after diluting with water, I filtered off the mixture of silica and silicon. I dried the filter, scraped from it its contents, and, after burning it, I added filter contents and filter ashes together, and treated them for 24 hours with strong hydrofluoric acid, in order to dissolve the silica and the iron silicide. The remaining silicon was fused with soda and saltpeter, and the silicon and iron were determined by the usual methods. I say iron was determined, because small amounts, mostly very small and not over 0.15 per cent., often withstand the action of the hydrofluoric acid. This iron was supposed to be present as the compound $FeSi_2$, and a corresponding amount of silicon was deducted from the insoluble silicon that was found. By this method the results are more accurate than by simply weighing the insoluble silicon, for in the latter case the presence of any graphite or other matter insoluble in hydrofluoric acid impairs the value of the result. I obtained the following results:

	I.	II.	III.
Total silicon	55.67	39.14	41.53
Copper	43.83	60.32	57.40
Iron	0.50	0.67	0.42
Calcium	....	....	1.08
Insoluble silicon	47.00	28.61[1]	27.50

Sample I was very pure and was picked out with great care with the help of a strong glass. Samples II and III contained more or less of the surrounding micro-crystalline mass in which the crystals are imbedded.

[1] Average of two analyses, the results of which agree well with each other.

The copper determination of No. 1 was lost, for which reason the percentage of copper was found by deduction. Assuming that iron and calcium are present in the form of $CaSi_2$ and $FeSi_2$,[1] I calculate the relative amounts of copper and of silicon combined with it as follows:

	Found.			Calculated for
	I.	II.	III.	Cu_2Si.
Cu	84.29	85.95	82.61	81.71
Si	15.71	14.05	17.39	18.29

It appears from these analyses that where a large excess of silicon is present, as in these crystals, no silicides are formed that contain more silicon than the compound Cu_2Si. There is even less silicon united with the copper than would be the case if the latter were present only in the form of Cu_2Si. It is possible either that a part of the copper is present as a silicide containing less silicon, or a part of the copper may be in the free condition. In order to find this out I examined Sample No. II, which apparently contains the largest excess of copper. I rubbed a part of the finely pulverized material with mercury in a mortar. The mercury was then pressed through four layers of linen until it proved to be free from adherent particles of crystals when examined with a glass. The mercury was now evaporated from a porcelain crucible. It left a considerable deposit of cuprous oxide, which dissolved with a green color in strong hydrochloric acid, and was further detected by the usual reagents, *i. e.*, ammonia and potassium ferrocyanide. It had been previously ascertained that the mercury which was used left no residue on evaporation.

It is not at all probable that mercury dissolves copper unless the latter is in the free condition. The mercury, moreover, did not dissolve silicon and, that it should decompose a silicide, if simply rubbed with it in a mortar, seems still more improbable. In the same manner I showed the presence of considerable amounts of free copper in an alloy containing 26 per cent. of silicon, the copper of which had been six hours in the furnace.

The result of this mercury test confirms the results of the

[1] See this JOURNAL, 18, 539.

analyses. We have here an interesting case where free copper, free silicon, and copper silicide exist side by side in the electric furnace. The copper had certainly time enough to combine with silicon, for in all cases it had been in the electric furnace for at least two hours. It might also be suggested that all the copper had not been in or very near to the arc, and that it unites with silicon only at such a place, but silicon and copper unite at a much lower temperature, for example in a blast furnace.

We seem to have here a case of chemical equilibrium between copper silicide, Cu_2Si, and its dissociation products, copper and silicon, which can be compared with the dissociation of carbonic acid into the monoxide and oxygen. So far as I know this is the first case of the kind observed in the preparation of carbides, silicides or other similar compounds in the electric furnace. From these results it seemed to me likely that free silicon should occur in silicon alloys containing less silicon than the compound Cu_2Si.

Vigoureux says that copper silicon alloys up to nearly 20 per cent. of silicon are quite homogeneous, and do not contain free silicon. I had previously found that *aqua regia* does not completely decompose alloys containing 13–14 per cent. of silicon. By further examination I found for example that a sample of alloy made in the electric furnace contained :

Total silicon	14.22
Free crystalline silicon	1.65

This agrees with my former deductions. I cannot say how far the difference in the method of preparation of the alloys has affected the results.

Vigoureux worked with mixtures of silicon and copper for a few minutes, and I heated a mixture of silica and carbon for several hours in a furnace with a copper cathode.

Iron Silicides.—Iron silicides of the following formulas have been described : Fe_2Si,[1] Fe_2Si_3,[2] $FeSi$[3] and $FeSi_2$.[4] Hahn obtained the latter compound by treating the impure silicide, Fe_2Si, with hydrofluoric acid, and he describes it as an insoluble residue. Moissan was unable to obtain a similar re-

[1] Hahn : Ann. Chem. (Liebig), **129**, 57 ; Moissan : Compt. rend., **121**, 621.
[2] J. Am. Chem. Soc., **17**, 923. [3] Hahn : loc. cit. [4] Hahn : loc. cit.

sult, which makes Hahn's statement appear doubtful. I had several reasons to believe in the existence of a compound $FeSi_3$, but I believed it to be soluble in hydrofluoric acid. I can easily obtain iron-silicon alloys containing 35–40 per cent. of silicon, which are entirely soluble in hydrofluoric acid, and therefore do not contain free silicon. I also obtained in the electric furnace an alloy containing 46.22 per cent. of silicon, which apparently did not contain free silicon, but I did not test at the time whether this alloy was soluble in hydrofluoric acid.

I now took an alloy of about 39 per cent. of silicon, pulverized it well, and, after having mixed it with water, I added a little hydrofluoric acid at a time, adding from time to time more water, and cooling the platinum dish all the time. After the most violent reaction was over, I allowed the dish to stand for 24 hours. I found in it a residue of gray, metallic crystals, which contained:

I.	II.	Calculated for $FeSi_3$.
48.26	49.71	50.16
52.24	50.56	49.84

The yield was small—about 20 per cent. The compound, $FeSi_3$, therefore, undoubtedly exists, and it finds its place beside the compounds, $MnSi_3$, $CrSi_3$ and $CaSi_3$. It is completely soluble in cold hydrofluoric acid, especially if the latter is concentrated, but it is less so than the iron silicides, which contain less silicon.

WILLSON ALUMINUM CO., SPRAY, N. C.
NOVEMBER, 1896.

Contributions from the Laboratories of the Massachusetts Institute of Technology.

XV.—FORMATION OF DIACETYLENYL (BUTADIINE) FROM COPPER ACETYLENE.

BY A. A. NOYES AND C. W. TUCKER.

In 1862 Reboul[1] found in passing acetylene into bromine that, in addition to the liquid bromides, there is often formed 6 to 8 per cent. of a crystalline substance. He did not further investigate it, but seems to have thought that it originated from impurities in his acetylene, which, how-

[1] Compt. rend., **54**, 1229.

ever, was prepared from copper acetylene and hydrochloric acid.

In 1875, and again in 1889, Sabanejeff[1] published accounts of quite extended investigations on the formation and properties of this bromide. The largest yield (6 per cent.) was obtained by passing acetylene (from copper acetylene) into boiling bromine. His analysis showed it to have the empirical formula C_2HBr_3, but a freezing-point determination of its solution in benzene showed that its molecular weight (500 and 504) was about twice that corresponding to this simple formula (265), and he therefore concluded that its symbol is $C_4H_2Br_6$. Molecular silver removed from the compound one-third of its bromine. As the bromide does not take up the full amount of bromine corresponding to bodies of the paraffin series, he believed it to be a ring compound, hexabromtetramethylene, and supposed it to be formed by the polymerization of bromacetylene, and subsequent addition of bromine.

The purpose of our investigation was to establish the constitution of this bromide, and to explain its origin. We first attempted to prepare some of it by passing acetylene generated from calcium carbide into boiling bromine until saturated, as Sabanejeff directs. Five experiments were made, each with a half pound or pound of bromine, the conditions being varied somewhat. In one experiment the bromine was covered with water; in another the acetylene was caused to combine with the bromine vapors above the liquid. But in no case could the slightest separation of crystals be observed, even on cooling the liquid product in a freezing-mixture, or after fractional distillation of it with steam. Acetylene from calcium carbide was then passed into ammoniacal cuprous chloride, the copper compound decomposed by hot hydrochloric acid, and the evolved gas passed into boiling bromine until it was decolorized. On cooling, a considerable quantity of crystals separated, constituting 4 per cent. of the total product. Their properties showed them to be identical with the bromide of Sabanejeff.

It is evident, from these experiments, that the crystals are

[1] Ann. Chem. (Liebig), **178**, 114; J. Russian Chem. Soc., **21**, 1; Ber. d. chem. Ges., **22 c**, 249.

not produced from pure acetylene, but from some other substance present in the gas resulting from the decomposition of copper acetylene by hydrochloric acid.

We next directed our attention to a study of the conditions which determine the yield of the solid bromide; for the quantity of it obtained varied greatly in different experiments, carried out apparently in exactly the same manner. For example, in five preparations, all made in the manner above described, the amounts of the solid bromide obtained were 2.1, 3.0, 4.0, 1.8, and 1.8 per cent. of the total product, which consisted of 387, 209, 125, 553, and 454 grams, respectively.

It was first determined that the crystalline bromide is formed in just as good yield (4 per cent.) when the copper acetylene is decomposed by potassium cyanide solution instead of hydrochloric acid. It seemed probable from this experiment that the bromide does not owe its origin primarily to the reaction of either of these reagents on copper acetylene, but to some other cause. No further light was thrown on the matter by a study of the effect of varying the conditions of the combination of the gas with the bromine. Better yields, consisting sometimes of 5 per cent., seemed to be obtained when smaller quantities of bromine were used.

The true explanation of the origin of the solid bromide finally became evident when it was discovered that the formation is entirely prevented by the addition of strips of metallic copper to the copper acetylene during its decomposition by the hydrochloric acid. The hydrocarbon corresponding to the bromide is therefore evidently produced by the oxidizing action of cupric chloride formed by contact of its decomposing mixture with the air. If this explanation is correct, the yield should be greatly increased by the direct addition of cupric chloride to the copper acetylene before its decomposition. And it was in fact found that such is the case, 9 per cent. of the crystals being obtained when an equal weight of crystallized cupric chloride was mixed with the copper acetylene. The following experiment was also tried: A measured volume of acetylene was passed into ammoniacal cuprous chloride solution until the latter was saturated; the precipitate was washed, water and an equal molecular quantity of

cupric chloride added to it, and the mixture (C_3Cu_3+$CuCl_2$+xH_2O) heated for three hours on a water-bath. At the end of that time the solution was decolorized, and the cupric chloride completely reduced.

The origin of the hydrocarbon being thus determined, it remained to establish its constitution. It seemed desirable first to confirm the composition and molecular weight assigned to the bromide by Sabanejeff. Analyses of a portion crystallized from boiling benzene, were made with the following results:

I. 0.4875 gram substance gave 0.1661 gram CO_2 and 0.0253 gram H_2O.

II. 0.5715 gram substance gave 0.1917 gram CO_2 and 0.0264 gram H_2O.

III. 0.5587 gram substance gave 1.180 gram AgBr.

	Found.			Calculated for	
	I.	II.	III.	$C_4H_2Br_6$.	$C_4H_4Br_6$.
C	9.29	9.15	9.26	9.07	9.04
H	0.58	0.52	0.53	0.38	0.76
Br	89.76	....	90.31	90.55	90.20

Column III contains Sabanejeff's results, which are seen to agree closely with our own. The percentage composition corresponds to that required by the formula $C_4H_2Br_6$. The formula $C_4H_4Br_6$ is out of the question, for it corresponds to over 0.2 per cent. more hydrogen than that actually found.

The confirmation of the molecular weight is even more important; for in the determination published by Sabanejeff the greatest observed lowering of the freezing-point was only 0°.08. The following determinations were made by Beckmann's boiling-point method, using as a solvent chloroform, whose molecular raising is 36°.6 according to Beckmann's[1] calculation.

Weight of chloroform taken, 40.68 grams.

Weight substance taken.	Weight substance in 100 grams solvent.	Rise in boiling-point.	Molecular weight found.	Calculated for $C_4H_2Br_6$.
0.639	1.570	0.108	532	530
1.335	3.282	0.227	529	....
1.806	4.439	0.292	556	....

[1] Ztschr. phys. Chem., 6, 445.

There is therefore no doubt that the molecular formula of the substance is $C_4H_2Br_4$, as stated by Sabanejeff.

Incidentally, at this point, the properties of our bromide may be noted. It melted at 183°.5 (corr.) (according to Sabanejeff at 172°–174°). It crystallized in colorless transparent plates belonging to the orthorhombic system. Crystallographic measurements, made for us by Prof. G. E. Barton, showed that the exterior angles were 264° 30′, 303° 30′, and 48° 45′, the prism angle 120° 40′, and that between the brachypinacoid and prism face 57° 15′. When the substance is heated above its melting-point, bromine vapors are evolved; and at 220° under a pressure of 40 mm. a liquid distils over, which recombines partially with the bromine vapors to form the original solid bromide.

We will next consider the constitution of this bromide and the nature of the hydrocarbon from which it is derived. Owing to the fact that, although produced in the presence of a large excess of boiling bromine, it takes up two atoms less than corresponds to saturation,[1] Sabanejeff concluded that it was hexabromtetramethylene, a compound with a closed ring. Since our experiments prove that it is not produced at all when pure acetylene is passed into bromine, his explanation of its formation by the polymerization of bromacetylene is obviously incorrect. It is, however, possible that hexabromtetramethylene might be formed from the closed-ring hydrocarbon $(CH)_4$, a polymer of acetylene, by the substitution of two atoms and the addition of four atoms of bromine. There are, however, two facts which conclusively prove that the bromide does not owe its origin to this hydrocarbon. One is that the hydrocarbon forming the bromide is an *oxidation-product* of acetylene or its copper compounds, as shown by the copper and cupric chloride experiments above described. The other is that the gas evolved from the copper acetylene was several times examined, and in every case found to be completely absorbed by ammoniacal cuprous chloride, thus showing it to consist only of triple-bonded compounds.

[1] We found, moreover, that even when heated to 140° in a closed tube with a large excess of bromine, the bromide remained entirely unaffected, as was shown by the unchanged melting-point.

The only explanation consistent with these facts is, therefore, that the bromide is formed by the direct union with bromine of the hydrocarbon, C_4H_2, diacetylenyl, or butadiine, and that the latter is formed from copper acetylene by the following reactions:

$$2C_2Cu_2 + 2CuCl_2 = C_4Cu_2 + 2Cu_2Cl_2.$$
$$C_4Cu_2 + 2HCl = CH \vdots C.C \vdots CH + Cu_2Cl_2.$$

It has been shown by Griner[1] that an entirely similar reaction takes place when copper allylene is treated with potassium ferricyanide.

That the hydrocarbon combines only with six atoms of bromine, and not with eight, is to be explained by the principle that halogen compounds which contain as large a proportion of halogen as the hexabromide, even though theoretically unsaturated, have very little tendency to combine with more halogen. In exemplification of this principle, reference may be made to the fact that tetrabromethylene, C_2Br_4, is met with as a product of energetic brominations.[2]

Diacetylenyl has been already obtained by Baeyer[3] from diacetylenedicarbonic acid, but not in sufficient quantity for analysis or determination of its properties. We therefore attempted to separate it from the gas prepared from copper acetylene by passing it through a worm, surrounded by a freezing-mixture. In this way a few cubic centimeters of a liquid were condensed, which boiled from 40°–50° and gave, with bromine, crystals of diacetylenyl hexabromide. But the condensed product contained also a large proportion of a chlorine compound, from which the hydrocarbon could not be separated by distillation.

[1] Beilstein's Handbuch, 1, 140.

[2] See Beilstein's Handbuch der organischen Chemie; also, Ber. d. chem. Ges., 11, 2238.

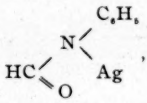
[3] Ber. d. chem. Ges., 18, 2272.

Contribution from the Sheffield Laboratory of Yale University.

XLVIII.—ON THE ACTION OF ACID CHLORIDES ON THE IMIDO ESTERS AND ISOANILIDES, AND ON THE STRUCTURE OF THE SILVER SALTS OF THE ANILIDES.

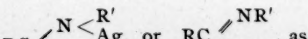
By H. L. Wheeler and P. T. Walden.

It has been shown in recent papers[1] from this laboratory that the silver salts of the anilides react with acid chlorides, giving diacid anilides, and, therefore, as if they had the structure

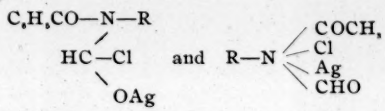


provided the action be considered as a direct replacement or double decomposition. The conclusion that follows from these reactions, with the above proviso, *i. e.*, that the silver salts have the metal joined to nitrogen, is directly opposite to that obtained by the action of alkyl halides.[2] In the latter case it was concluded that the metal was joined to oxygen, since isoanilides or substituted imido ethers were obtained.

These contradictory reactions are certainly not to be dismissed with the statement that they are due to tautomerism. The products obtained by acting on the silver salts with acid chlorides retained silver halide persistently, and it was considered possible that *the reaction was not a double decomposition, but that it took place first by addition then separation of silver halide*. Two forms of addition-products were considered, according to whether the silver salts are derivatives of the type



, as follows:



A. B.

[1] Wheeler and Boltwood: This Journal, 18, 381; *Ibid.*, 696.

[2] Comstock and Kleeberg: This Journal, 12, 495.

Before proceeding to the discussion of the probable structure of the silver salts, it is evidently desirable to study the action of acid chlorides on compounds that are definitely constituted according to one of the above types. The isoanilides and the free imido esters were therefore selected with the object of determining in what manner the acid chlorides would react with compounds which undoubtedly contain the atomic grouping $RC\begin{matrix}\diagup\!\!\!= NR' \\ \diagdown OR''\end{matrix}$ since this grouping is generally assumed to exist in the silver salts of the amides and anilides.

We find that the reaction takes place readily at ordinary temperatures and goes quantitatively in two ways, according to whether the imido group in the imido ester is substituted or not.

The Action of Acid Chlorides on the Isoanilides.

The substituted imido esters or isoanilides react with acid chlorides as follows:

$$HC\begin{matrix}\diagup\!\!\!= NC_6H_5 \\ \diagdown OCH_3\end{matrix} + ClCOC_6H_5 = HC\begin{matrix}\diagup N\!<\!\begin{matrix}C_6H_5 \\ COC_6H_5\end{matrix} \\ \diagdown\ Cl \\ \quad\ OCH_3\end{matrix}.$$

This intermediate addition-product immediately decomposes with the evolution of methyl chloride and a mixed diacid anilide results:

$$HC\begin{matrix}\diagup N\!<\!\begin{matrix}C_6H_5 \\ COC_6H_5\end{matrix} \\ \diagdown\ Cl \\ \quad\ O\,CH_3\end{matrix} = HC\begin{matrix}\diagup N\!<\!\begin{matrix}C_6H_5 \\ COC_6H_5\end{matrix} \\ \diagdown\!\!\!= O\end{matrix} + CH_3Cl.$$

The mixed diacid anilides thus obtained decompose with alkali, giving the mono acid anilide of the higher acid group, thus showing that they have both acid groups attached to nitrogen. That the isoanilides react so readily with acid chlorides is due to the double union between carbon and nitrogen, since, were it otherwise, the acid chloride would

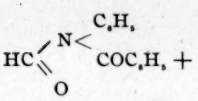
have to act by double decomposition on the group $-\overset{\|}{C}-OCH_3$. Such a direct double decomposition is evidently impossible, since it has been found that one of the characteristic properties of the group $-\overset{\|}{C}-OCH_3$ is that it is *not* acted on by acid chlorides. Indeed on this fact is based the general method of determining the presence or absence of this group in compounds which may contain either this or hydroxyl. In such cases, as is well known, the latter alone reacts with acid chlorides. That this reaction is not a direct double decomposition or replacement of the alkyl group by the acid radical is also shown by the fact that non-substituted imido esters react with acid chlorides with the separation of hydrogen chloride instead of alkyl chloride (see below). It is at once evident that the only reaction which will explain the different behavior of the imido esters and isoanilides toward acid chlorides, and which will be general for both cases is that of addition.

The reactions of acid chlorides on the isoanilides and imido esters are the first that have been obtained, in the case of substances that have, or are supposed to have, the structure $RC\begin{matrix}\diagup\!\!\diagup NR' \\ \diagdown OR''\end{matrix}$, which admit of only one general interpretation, and in which the so-called tautomerism or wandering of groups is excluded. They show that the so-called tautomeric or contradictory reactions in the case of the silver salts are to be explained by addition.[1] We are now in a position to discuss the structure of the silver salts.

It is to be noticed that the above reactions of the isoanilides are perfectly analogous to the action of the acid chlorides on the silver salts of the anilides, and the course of the reaction in the latter case is, therefore, to be interpreted as follows, the addition taking place according to type A as given above:

$$HC\begin{matrix}\diagup\!\!\diagup NC_6H_5 \\ \diagdown OAg\end{matrix} + ClCOC_6H_5 = HC\begin{matrix}C_6H_5CO-N-C_6H_5 \\ \diagup \\ \diagdown Cl \\ \diagdown O\,Ag\end{matrix} =$$

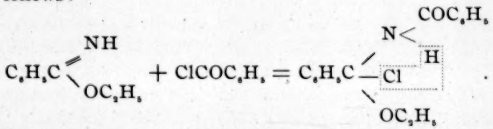
[1] Compare Nef: Ann. Chem. (Liebig), **270**, 293.



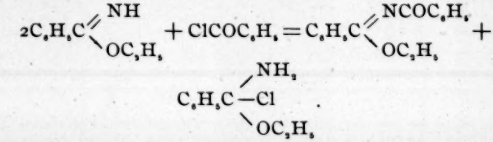
From which it follows that the silver salts of the anilides have the metal joined to oxygen as first stated by Comstock and Kleeberg.[1]

The Action of the Acid Chlorides on the Imido Esters.

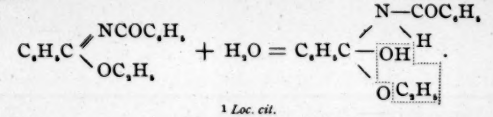
The non-substituted imido esters react with acid chlorides as follows:



This intermediate addition-product, like the preceding, immediately decomposes, not however with the evolution of ethyl chloride, as in the case of the isoanilides, but by separation of hydrogen chloride. (Since chlorine has a greater tendency to unite with hydrogen than with methyl or alkyl.) The hydrogen chloride liberated in this manner combines with the excess of imido ether, and the products obtained are formed as follows:



When the acyl imido esters are treated with acid, or when they are exposed to the air for some time, they take up a molecule of water and decompose into diacid amides as follows:



[1] *Loc. cit.*

The above decomposition is perfectly analogous to the action of the silver salts of the amides[1] and anilides[2] with acids, and finally this decomposition proves that the diacid amides—like the diacid anilides—have both acid groups attached to nitrogen, and the statement no longer holds true that diacid amides of the type R—CONHR′ are still unknown,[3] or that in the present state of our knowledge dibenzamide may have the structure[4] $C_6H_5C\begin{matrix}\diagup NH \\ \diagdown OCOC_6H_5\end{matrix}$.

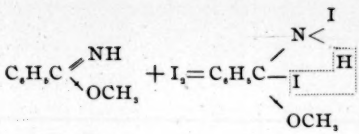
In fact diacid amides of the latter type, with the acyl group attached to oxygen are probably incapable of existence. This conclusion has been reached through the following considerations: It has been shown in a recent paper[5] from this laboratory that silver benzamide reacts with acid chlorides, giving benzonitrile, and therefore differently from the silver salts of the anilides, which give diacid anilides.[6] It has been shown above that in all probability the action of acid chlorides on silver formanilide takes place by addition. Therefore, in the case of benzamide, it must be double decomposition. (This was previously stated as the only simple explanation.) The resulting isodiacid amide is formed and breaks up as follows:

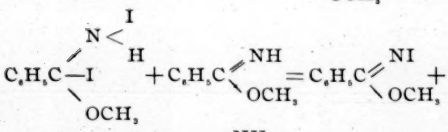
$$C_6H_5C\begin{matrix}=NH \\ \diagdown OAg\end{matrix} + RCOCl = C_6H_5C\begin{matrix}\diagup N\,H \\ \diagdown OCOR\end{matrix} + AgCl.$$

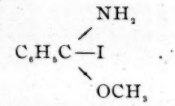
The Action of the Halogens on the Imido Esters. Halogen Imido Esters.

So far only the action of bromine and iodine have been tried. The result is precisely similar to that of the action of acid chlorides, two molecules of the imido ester react with one molecule of halogen, giving halogen imido esters and halogen hydride salts of imido ester, most likely as follows:

[1] Tafel and Enoch: Ber. d. chem. Ges., **33**, 105.
[2] Comstock and Clapp: This JOURNAL, **13**, 525.
[3] Pinner: *Die Imidoäther und ihre Derivate*, p. 9.
[4] Pinner: Ber. d. chem. Ges., **25**, 1436.
[5] Wheeler: This JOURNAL, **18**, 701.
[6] Wheeler and Boltwood: *Loc. cit.*







EXPERIMENTAL PART.

Formylacetanilide, $C_6H_5N<^{CHO}_{COCH_3}$.—Acetyl chloride reacts on phenylformimidoethyl ester[1] at ordinary temperatures with a violent evolution of ethyl chloride. It is best to modify the reaction by diluting with a dry solvent. The following procedure proved satisfactory: Five grams of imido ester were mixed with 5.6 grams of acetyl chloride in a mixture of ether and ligroïn. The evolution of ethyl chloride took place smoothly and a colorless oil separated. The whole was allowed to stand for 12 hours. The oil was then taken up with ether and shaken with a solution of sodium bicarbonate. On evaporating off the ether an oil was obtained which, after standing several days, was distilled at 23 mm. pressure, when practically the entire quantity distilled from 157° to 158°. It was then cooled in a freezing-mixture and, on stirring, it solidified. After pressing on a porous plate, it was crystallized from a mixture of ether and ligroïn, when beautiful, thick, brittle crystals were obtained melting from 56° to 57°. This material proved to be identical with formylacetanilide obtained from silver formanilide and acetyl chloride.[2] On

[1] Prepared from the silver salt of formanilide and ethyl iodide: Comstock and Kleeberg, This JOURNAL, *loc. cit.*

[2] This JOURNAL, 18, 698.

treating it with sodium hydrate, acetanilide was formed.

Formylbenzanilide, $C_6H_5N<^{CHO}_{COC_6H_5}$.—On mixing molecular proportions of phenylformimidoethyl ester and benzoyl chloride, the reaction takes place more quietly than in the previous case. After the evolution of ethyl chloride ceases the material gives needles. When crystallized from alcohol these melt at 112°, and in other respects are identical with the products obtained from silver and mercury formanilide with benzoyl chloride. When treated with sodium hydrate it gives benzanilide. It was stated in a previous paper[1] that "a mixture of benzanilide and formylbenzanilide can readily be distinguished when crystallized from alcohol. The former separates first in needles; the latter forms a supersaturated solution, and on shaking deposits plates." This is a mistake, as it is just the reverse. The formylbenzanilide is the least soluble and comes down first in needles.

Formylbenzenesulphonanilide, $C_6H_5N<^{CHO}_{SO_2C_6H_5}$.—Phenylformimidoethyl ester and benzene sulphochloride react slowly at ordinary temperatures. Four grams of the imido ether and 4.7 grams of benzene sulphochloride were mixed and kept at a temperature of about 38° to 43° for two days. The mixture then became semi-solid. It was washed with alcohol and the residue crystallized from strong alcohol, when beautiful, colorless, radiating needles were obtained. These melted at 148°–149°. This material on analysis gave the following results:

	Found.	Calculated for $C_{13}H_{11}NO_3S$.
N	5.2	5.3

Half a gram of the analyzed material was boiled with a 10 per cent. solution of sodium hydrate. Solution took place, and on cooling, nothing separated; dilute hydrochloric acid was then added, and the resulting colorless precipitate was washed with water and dried in the air. It melted at 110° without further purification. This was therefore benzenesulphonanilide. In the case of this mixed diacid anilide, as

[1] Wheeler and Boltwood: This JOURNAL, 18, 381.

well as in all previous cases, alkali first removes the lower acid group.

Formylbenzorthotoluide, $CH_3C_6H_4N<^{CHO}_{COC_6H_5}$.—Molecular proportions of orthotolylformimidomethyl ester and benzoyl chloride were mixed, and the whole heated to 80° until the evolution of methyl chloride had stopped. The mass was then poured into a little alcohol, when rectangular, colorless, shining plates separated. These melted at 91°, and when carefully crystallized from strong alcohol the melting-point did not change. The melting-point of this compound is therefore 91° and not 92°, as previously stated.[1] It gave benzorthotoluide when treated with alkali.

Formylbenzparatoluide, $CH_3C_6H_4N<^{CHO}_{COC_6H_5}$.—This was prepared from paratolylformimidomethyl ester in the same manner as the preceding compound. It was identical with the compound prepared from mercury formparatoluide and benzoyl chloride.[2] Its melting-point is more nearly 102° than 101°, as previously stated. When treated with alkali it gave benzparatoluide. A similar decomposition into the monoacid anilide is slowly caused when this and the preceding compound are boiled with dilute alcohol.

Acyl Imido Esters.

Benzoylimidoethyl Benzoate, $C_6H_5C<^{NCOC_6H_5}_{OC_2H_5}$.—When benzimidoethyl ester and benzoyl chloride[3] are mixed (in ethereal solution) in the proportion of two molecules of the former to one of the latter, and allowed to stand for 12 hours, snow-white needles separate. These consist of the hydrochloride of benzimidoethyl ester. On filtering and concentrating the ethereal solution, colorless, spear-like or lozenge-shaped crystals separate. These were carefully crystallized from dilute alcohol for analysis. The pure material thus obtained melted at 65°.

[1] Wheeler and Boltwood: This JOURNAL, **18**, 381.

[2] Wheeler and McFarland: This JOURNAL, **18**, 540.

[3] The pure benzimidoethyl and methyl esters for this work were prepared according to Bushong's excellent method. This JOURNAL, **18**, 490.

	Found.	Calculated for $C_{16}H_{15}NO_3$.
C	76.3	75.9
H	6.1	5.9
N	5.5	5.5

Benzoylimidoethyl benzoate is stable towards alkali in the cold; acids on the other hand readily convert it into dibenzmide. When the dilute alcoholic solution is warmed with a few drops of dilute sulphuric acid, needles of the diacid amide are obtained, melting at 148°.

Acetylimidomethyl Benzoate, $C_6H_5C\begin{matrix}\diagup\!\!\diagup NCOCH_3\\ \diagdown\!\!\diagdown OCH_3\end{matrix}$.—Benzimidomethyl ester and acetyl chloride, in the proportion of two molecules of the former to one of the latter, were mixed in ethereal solution. After 12 hours the hydrochloride of the imido ester was filtered off, and on evaporating the ether an oil was obtained. This was distilled at 20 mm. pressure, when about one-third passed over below 140°, and the remainder at about this temperature. The portion boiling at 140° was redistilled at 15 mm. A few drops were removed below 139°, and then the remainder boiled almost entirely at this temperature. This fraction on cooling in a freezing-mixture did not solidify. It was analyzed with the following result:

	Found.	Calculated for $C_{18}H_{11}NO_3$.
N	8.12	7.91

The portion mentioned above, boiling below 140°, consisted of unaltered imido ester and benzonitrile (?). When acetylimidomethyl benzoate is mixed with a little alcohol and a few drops of dilute sulphuric acid added, evolution of heat occurs and the whole on cooling solidifies to a mass of colorless prisms or needles. This material is acetylbenzamide, which melts at 120°.[1]

Acetylimidoethyl Benzoate, $C_6H_5C\begin{matrix}\diagup\!\!\diagup NCOCH_3\\ \diagdown\!\!\diagdown OC_2H_5\end{matrix}$. — This was prepared from benzimidoethyl ester and acetyl chloride in the same manner as the above acylimido esters. The ethereal solution was washed with dilute sodium hydroxide and water.

[1] Pinner: Ber. d. chem. Ges., **23**, 1436.

On evaporation, an oil was obtained which was distilled at 13 mm. pressure. About one-third was collected below 140°.5 and the remaining two-thirds from 140°.5 to 147°.5.

The larger portion was again distilled at 17 mm., when the greater part boiled at 151°. A nitrogen determination of this gave the following result:

	Found.	Calculated for $C_{11}H_{13}NO_3$.
N	7.65	7.33

When acetylimidoethyl benzoate is treated with dilute sulphuric acid, as described in the case of the methyl compound, it is converted into acetbenzamide with evolution of heat.

Halogen Imido Esters.

The first representatives of this class of compounds in the benzoic acid series have just been prepared by Stieglitz,[1] who describes chlorimidoethyl benzoate and bromimidoethyl benzoate. He obtained these compounds by acting on the imido ester hydrochlorides with sodium hypochlorite and hypobromite. These interesting compounds were obtained as oils which in the case of the chlorine compound was found to distil unchanged at 16 mm. pressure.[2]

We have found that bromimidomethyl benzoate and the analogous iodimidomethyl ester result, along with other products, by directly combining the free esters with the halogen.

Bromimidomethyl Benzoate, $C_6H_5C\begin{matrix}=NBr\\ \diagdown OCH_3\end{matrix}$.—This was obtained as a pale yellow oil of pleasant odor, which can be distilled below 20 mm. pressure. It reacts with strong aqueous ammonia with effervescence, giving off nitrogen. Dilute hydrochloric acid evolves bromine. It is therefore identical in properties with its homologue bromimidoethyl benzoate described by Stieglitz.

Iodimidomethyl Benzoate, $C_6H_5C\begin{matrix}=NI\\ \diagdown OCH_3\end{matrix}$. — Iodine reacts with benzimidomethyl ester very slowly. After warming the mixture on the water-bath for several days the mass was ex-

[1] This JOURNAL, 18, 751.

[2] It is interesting to note the great stability of this substituted nitrogen chloride.

tracted with ether, the ether shaken with solid potassium hydrate, and the uncombined iodine removed. On evaporating off the ether in a vacuum desiccator over potassium hydrate, the iodimidomethyl benzoate was obtained as a light yellow oil, mixed with unaltered imido ester. A small amount of colorless needles separated. They were insoluble in water and boiling alcohol. They melted from 222° to 228° and were probably triphenyltricyanide or cyaphenin. When the above oil was treated with strong ammonia it turned black from the separation of iodine. Dilute nitric acid gave the same result. On attempting to distil the crude product at 13 mm. pressure, it decomposed with the separation of iodine.

Owing to the appearance of Dr. Stieglitz's paper, and since he states his intention of further investigating these compounds, the work on the halogen imido esters has been abandoned by us at this point. We desire to reserve the work on acyl imido esters for ourselves, and, it is our intention to investigate the action of other acid chlorides on the imido esters and isoanilides, and also to examine the reactions of the acyl imido esters more thoroughly.

NEW HAVEN, NOVEMBER, 1896.

ON THE EFFECT OF LIGHT ON THE DISPLACEMENT OF BROMINE AND IODINE FROM ORGANIC BROMIDES AND IODIDES.

BY J. H. KASTLE AND W. A. BEATTY.

The halogen derivatives of the sulphonamides have been under investigation in this laboratory for some time. It has been found that these compounds are readily decomposed by heat and chemical reagents of various kinds. While studying their properties it occurred to one of us (Kastle) to test their behavior towards light. A small quantity of the dibrom derivative of benzenesulphonamide, $C_6H_5SO_2NBr_2$, was exposed to the sunlight in a sealed tube. After remaining exposed to the light for a short time, it was observed that decomposition of the compound had taken place, whereby a considerable quantity of bromine vapor was observed to have been set free. A small amount of the bromine compound was next placed in a tube with a small quantity of water, and the

tube sealed and exposed to the sunlight. Bromine vapor again made its appearance, filling the upper part of the tube, thereby indicating that the compound had been decomposed by light even in the presence of water. The decomposition of this class of compounds by light has been found to be more deep-seated than it was at first thought to be, as the result of which this subject is still under investigation. Our study of this decomposition, however, while not complete in itself, has incidentally led to some interesting observations as to the displacement of bromine and iodine from their most stable compounds. The first clue that such displacement can be brought about was furnished by the conduct of the dichlor derivative of *p*-brombenzenesulphonamide, $BrC_6H_4.SONCl_2$, towards sunlight. This substance was placed in a tube, together with a small amount of water; the tube was then sealed, and exposed to the direct sunlight. After standing for some time it was seen that chlorine had been set free. The tube was then allowed to remain exposed to the direct sunlight for several days longer, when it was observed that bromine vapor had made its appearance in the place of chlorine. This, of course, indicated that the chlorine, after its liberation from the compound, had reacted with the substance remaining so as to set free bromine from the benzene ring. This reaction seemed so remarkable in certain respects that it was deemed expedient to make still other experiments along this line. The question of course suggested itself in this connection, could chlorine thus evolved effect the displacement of bromine or iodine in general or only from the original molecule of which it had formed a part? In order to test this point the following experiments were tried:

I. Benzenedibromsulphonamide and iodoform were brought together with a little water in a sealed tube and exposed to the sunlight for several days. An abundance of iodine was set free.

II. *p*-Toluenedichlorsulphonamide and iodoform gave a result similar to that obtained in I., except that the reaction took place more slowly.

III. *p*-Toluenedichlorsulphonamide and *p*-iodobenzoic sulphinide, together with water, were exposed to the light in a

sealed tube from Sept. 26 to Oct. 20. The solution contained an abundance of free iodine, as was shown by its color and by filtering and shaking with carbon disulphide.

IV. *p*-Toluenedichlorsulphonamide and *p*-dibrombenzene were allowed to stand under water exposed to the sunlight from Sept. 26 to Oct. 21. After filtering the solution gave a very distinct test for bromine.

V. *p*-Toluenedichlorsulphonamide with the compound

$$C_6H_4<\begin{matrix}SO_2OC_2H_5\\ I(p)\end{matrix},$$

under water, stood in sunlight nearly all the time from Sept. 25 to Oct. 30. On Oct. 29, it was observed that the water above the insoluble ether was slightly colored. On Oct. 30 this color became very distinctly brownish yellow. The tube was opened and the contents filtered. Carbon disulphide was added to the filtrate. An excellent test for iodine was obtained. The ether that remained was colored pink.

VI. Benzenedibromsulphonamide and *p*-iodosulphinide and water were exposed to light from Nov. 3 to Nov. 11. The presence of free iodine was easily detected.

VII. Barium *p*-iodobenzenesulphonate and benzenedibromsulphonamide in water were exposed to light in a sealed tube from Nov. 3 to Nov. 11.

A test showed the presence of considerable free iodine.

The following experiments were tried in the dark.

I. *p*-Toluenedichlorsulphonamide and iodoform in a small quantity of water were kept in the dark from Sept. 25 to Nov. 19. Only a faint test for iodine was obtained.

II. *p*-Brombenzenedichlorsulphonamide in a little water was kept in the dark from Sept. 26 to Nov. 19. No test for bromine.

III. *p*-Toluenedichlorsulphonamide and dibrombenzene, in a little water, was kept in a sealed tube in the dark from Sept. 26 to Nov. 19. No test for bromine.

IV. *p*-Brombenzenedichlorsulphonamide and iodoform in a little water, were kept in the dark from Sept. 26 to Nov. 19. Good test for iodine.

It thus appears that the chlorine liberated from the dichlorsulphonamides by the action of light can displace bromine

and iodine from their most stable compounds, and that the bromine of the dibromsulphonamides, when liberated, can displace iodine even from the benzene ring. Whereas in the dark, there being no liberation of the chlorine from the dichlorsulphonamide there is no displacement of the bromine or iodine from the organic halide, except from unstable compounds like iodoform; and with this substance it seems that a direct reaction takes place.

Action of Chlorine Water on Organic Bromides and Iodides.

The action of chlorine[1] water itself was next tried upon the following brom and iodo compounds; *viz.*, tetraiodopyrrol, ethyl *p*-iodobenzenesulphonate, *p*-iodobenzoic sulphinide, barium *p*-iodobenzenesulphonate, potassium *p*-brombenzenesulphonate, tribromphenol, *p*-dibrombenzene. The mode of procedure was as follows: About 0.2 gram of the iodo or brom compound was brought together in a test-tube with 5 cc. of chlorine water; the tube was then sealed and exposed to the light. Three of these tubes, *viz.*, those containing the tetraiodopyrrol, *p*-iodosulphinide. and barium *p*-iodobenzenesulphonate were exposed for nine days, from the 2nd to 11th of November. The experiment with the ethyl *p*-iodobenzenesulphonate was continued until Nov. 14, having an exposure of twelve days. That with the potassium *p*-brombenzenesulphonate was concluded on Nov. 12, having had an exposure of ten days.

In some of our experiments with tribromphenol this substance and the chlorine water were simply shaken together. Other experiments with this substance had an exposure of several hours. So with *p*-dibrombenzene, experiments with chlorine water were tried in which the exposure ranged from half an hour to several days.

These experiments were concluded by testing for bromine or iodine,[2] and, in every instance, an excellent test for either

[1] The chlorine water used in the experiments herein described was freshly prepared for each experiment or set of experiments. Usually the solution was about $\frac{N}{10}$.

[2] The test for bromine or iodine in these and the other experiments herein described was conducted in the following manner. After the desired exposure to light, the tube was opened and its contents filtered. The filtrate was shaken with a little zinc dust and again filtered. To this filtrate there was added a little chlorine

bromine or iodine was obtained, showing that chlorine in aqueous solution had effected the displacement of the bromine or iodine.

These results certainly go to show that bromine and iodine are displaced from even their most stable organic compounds by means of chlorine in aqueous solution, even in the case of compounds, which are practically insoluble in water. The ease with which this displacement takes place varies of course, and that too very considerably, with the nature of the iodo or brom derivatives. With compounds, such as propyl iodide, tribromphenol, etc., it was only necessary to shake the compound with chlorine water in order to have the setting free of iodine or bromine begin at once. Others, such as the ethyl *p*-iodobenzenesulphonate, seemed to require prolonged action of the chlorine before the iodine made its appearance.

On the Effect of Light upon the Reaction between Chlorine with Water and Organic Halides.

Still more remarkable is the effect of light upon the reaction. This effect is noticeable with the *p*-iodobenzoic sulphinide. After nine days the tube containing this compound and the chlorine water, which had been exposed to the sunlight, gave a very distinct test for iodine; whereas, a second tube, exactly like the first in contents, but which had been kept in the dark, showed at the best but a very faint trace of iodine.

The effect of light is still better shown in the experiments with *p*-dibrombenzene and chlorine water. In one of our earlier experiments along this line, two sealed tubes were prepared, each containing about 0.1 gram dibrombenzene and 5 cc. chlorine water. One of these was exposed to the light and kept immersed in running water, the temperature of which was 11°.5 to 13°.5 C. The other tube was kept in the dark. At the end of four hours the tubes were opened, their contents fil-

water or *p*-toluenedichlorsulphonamide[2] and carbon bisulphide. If, under these conditions, either the color of bromine or iodine was imparted to the carbon bisulphide it indicated that the displacement of one or the other of these halogens had been effected.

[2] The use of *p*-toluenedichlorsulphonamide in this connection is similar to that of benzenedichlorsulphonamide, which has been proposed as a reagent for bromine and iodine.

tered, and the filtrates tested for bromine. The one that had been exposed to the light gave a very distinct test for bromine, whereas, that which had remained in the dark showed no traces of bromine. The day on which these experiments were tried was alternately fair and cloudy, but mostly cloudy, so that the tube exposed to the light was in only diffused light during the greater part of the time, and yet this was sufficient to cause the decomposition. Still more conclusive results were obtained in a series of experiments begun Nov. 10, at 2.45 P.M., and conducted as follows: 0.2 gram dibrombenzene, together with 10 cc. chlorine water, were placed in a small glass-stoppered bottle. Six of these bottles having been thus prepared, three of them were placed in the direct sunlight and three kept in the dark. On Nov. 11, at 2.30 P. M., one of the bottles which had been exposed to the light was compared with one of those which had been kept in the dark. The difference was easily seen. The liquid in the bottle which had been exposed to the light was decidedly yellow, and a small quantity of yellowish-red vapor filled the upper part of the bottle. After filtering, the liquid gave an abundant test for bromine. On the other hand, the liquid in the bottle which had been kept in the dark was colorless, with not a trace of yellowish-brown vapor in the upper part of the bottle, and when tested for bromine it gave only a trace. In order to make sure of this point another one of the bottles which had been kept in the dark was opened and tested for bromine, with like result. It should be remarked, further, in this connection, that the afternoon of Nov. 10 was cloudy during the greater part of the time, and that Nov. 11 was also cloudy, so that the exposure to direct sunlight was short. Of the two bottles which were left exposed to the light at the conclusion of the first test, one was broken by accident, the third bottle was left exposed until Nov. 12, at 3.30, when this series of experiments was completed. At 3.30, Nov. 12, the bottle which had been exposed to the light since Nov. 10, 2.45 P.M., was compared with the bottle which had been kept in the dark since that time. The difference was very striking. The liquid in the bottle which had been exposed to the light was distinctly yellowish-red and vapors of bromine filled the

upper part of the bottle. In fact, bromine was so abundant as to need no test to confirm its presence. In the bottle which had been kept in the dark the liquid was as colorless as water. No bromine vapor could be seen in the bottle, and when its contents were filtered and tested, they gave only the slightest traces of bromine.

By reference to the record of the weather,[1] which was kept during this time, it will be observed that even this bottle, which was exposed to the light for the longest period, was in the direct sunlight only during the last day of exposure. In order to determine whether it was the heat or the light of the direct sunlight that caused the acceleration in the action of chlorine water on *p*-dibrombenzene, a tube containing 0.2 gram of the dibrombenzene and 5 cc. of chlorine water was immersed in running water, the temperature of which varied from 14° to 18° C., and was exposed to the direct sunlight for six hours. At the end of this time it could be easily observed that the reaction had taken place. The liquid in the tube had a decided yellowish-red color, and on being filtered and shaken with carbon bisulphide it gave an abundant test for bromine. This shows that the sunlight at 14°–18° C. is capable of working this change. In order, further, to make sure of the effect of an increase in temperature on the progress of the reaction, a tube containing the same quantities of dibrombenzene and chlorine water was exposed to the temperature of 50° C. in the dark, for five hours. When examined at the end of this time the liquid in the tube was seen to be colorless, and on filtering and testing for bromine it gave no test for this element. A similar tube was exposed to a tem-

[1] Record of weather for November, up to the time of writing:

Nov. 1, Fair.	Nov. 11, Cloudy.
" 2, Fair.	" 12, Fair.
" 3, Partly cloudy.	" 13, "
" 4, Cloudy.	" 14, Partly cloudy.
" 5, "	" 15, Fair.
" 6, Fair.	" 16, "
" 7, Cloudy.	" 17, Cloudy.
" 8, "	" 18, Partly cloudy.
" 9, Partly cloudy.	" 19, Cloudy.
" 10, Cloudy during greater part of day.	" 20, "

The last of the experiments herein described, involving exposure to light, was concluded on the 17th inst.

perature of 100° C., for five hours. After heating for this length of time it was allowed to remain in the dark all night at the ordinary temperature. When examined, it was found that the liquid in the tube was reddish-yellow. After filtering, the filtrate gave a splendid test for bromine. All these results, together with that described above, go to show that at ordinary temperature, and even up to 50° C., the reaction is not so much dependent on heat as it is on light. This, of course, does not mean that the reaction in question is uninfluenced by temperature. As a matter of fact, it has been observed that the reaction proceeds more rapidly at 30° C. in the sunlight than at 14° C, and, as has just been described, at 100° C. the action of the chlorine on the dibrombenzene takes place in the absence of light altogether. What is meant, rather, is that at ordinary temperatures light exerts an accelerating influence on the course of the reaction.

Still another experiment was tried, as follows, with the view of finding whether the chlorine actually replaced the bromine: 1 gram of pure dibrombenzene was placed in a small Florence flask, together with 100 cc. of chlorine water, containing 0.0057 gram chlorine per cc., or about twice the quantity required completely to displace the bromine from the dibrombenzene. The flask was then sealed and placed in the sunlight at 2.25 P.M., Nov. 6. The sun shone brightly during the entire afternoon. About an hour and a half after the beginning of the exposure to the sunlight, it could be clearly seen that some change was taking place. The liquid above the dibrombenzene was distinctly darker and of a more decided yellowish tint. Nov. 7 and 8 it was kept in one of the laboratory closets, and no further change in the color was observable. On Nov. 9 it was exposed to the light all day. It was very cloudy during the entire day and little if any change could be noted. It was also exposed all day on Nov. 10 and 11, both of which days were cloudy, except for a little while during the afternoon of the 10th. It could be seen, however, that the liquid had darkened a little in color. On the 12th the sun came out about 10.30, and shone brightly the rest of the day. During the first hour's exposure to the sunlight on this date it looked as if as great a change had taken place as

had occurred during all the preceding days of exposure. Vapor of bromine could be seen in the upper part of the flask. Nov. 13 was a fair day, the sun shining brightly during the entire day. This day's exposure seemed to complete the change, so far at least as the replacement of the bromine by the chlorine was concerned. The liquid in the flask had about the color of strong bromine water, and the upper part of the flask seemed saturated with bromine vapor. We allowed the flask to remain exposed to the light until the 17th. During the interval between the 13th and 17th about the only change observable was that the red color of the bromine became lighter, owing, doubtless, to its reacting with the water to form hydrobromic acid. On the 17th the flask was opened and its contents filtered. The filtrate was evaporated to dryness. Only a very small amount of solid residue was left, and this was not further examined. The white crystalline residue obtained on filtration was dried and weighed. It was found to weigh 0.6400 gram. The quantity of dichlorbenzene, which would be found if all the dibrombenzene were thus transferred is 0.6228 gram. The melting-point of the residue was found to be 55°–57°; that of dichlorbenzene is given as 55–56°.5. The residue was recrystallized from ether. The recrystallized product was not found to melt sharply, the melting-point being from 62°–66° C. The remainder of the substance was fused with a mixture of sodium carbonate and potassium nitrate. The fused mass was dissolved in water and the solution boiled with zinc dust. This was then filtered, and to the clear solution silver nitrate and nitric acid were added. The precipitate formed was shown to be a mixture of silver bromide and silver chloride. Hence the crystalline residue which is left after exposing *p*-brombenzene and chlorine water to the sunlight is either a mixture of *p*-chlor- and *p*-brombenzene or *p*-chlorbrombenzene, C_6H_4ClBr, a compound obtained by Körner[1] by the action of bromine on chlorbenzene, which is described as melting at 67° C.

Further work with larger quantities of material will be necessary definitely to settle this point. One thing, however,

[1] J., 1875, 319.

seems absolutely certain, and that is that some chlorine derivative is formed by the action of chlorine water in the sunlight on *p*-dibrombenzene, and that large quantities of bromine are set free. It seems probable that the chlorine not only displaces but replaces bromine and iodine in their aromatic derivatives.

It is believed that these results are new, especially those showing the accelerating influence of light upon the progress of the reactions studied.

No systematic study of the displacement of one halogen by another in organic compounds seems to have been made, and only a few scattering observations bearing upon this subject are to be found in the literature.

Dumas and Stas[1] have observed that chlorine gas acting on ethyl iodide gave ethyl chloride and free iodine. Geuther[2] has shown that ethyl iodide is converted into ethyl chloride by iodine chloride. Willgerodt[3] has shown that the compounds $C_6H_4Br.ICl_2$ and $C_6H_4ICl_2$ decompose alcoholic iodides with the setting free of iodine. Löscher[4] has observed that iodoform is changed to bromoform by the action of bromine. Then in the last edition of Watts' Dictionary, Vol. III, p. 31, is to be found the statement under the general remarks about iodo compounds that chlorine and bromine replace iodine directly.

Further, R. Meyer[5] has made the interesting observation that whereas chlorine and bromine replace iodine in isopropyl iodide yielding isopropyl chloride and bromide, respectively, *chlorine does not replace bromine in isopropyl bromide*. It is to be observed in this connection that R. Meyer allowed chlorine gas and pure bromine to act upon the organic halide in the dry state. It is conceivable, of course, that chlorine in aqueous solution and in the sunlight might be found to act more energetically upon this bromine derivative, a point which we hope to investigate as soon as possible.

It will be observed, therefore, that the results herein described are somewhat different from any that have ever been

[1] Ann. Chem. (Liebig), **35**, 162.
[2] *Ibid*, **123**, 123.
[3] J. prakt. Chem., [2], **33**, 154–158.
[4] Ber. d. chem. Ges., **21**, 410.
[5] J. prakt. Chem., [2], **34**, 104.

obtained, and it is believed that they are of sufficient interest to warrant publication in their present form. Still further work is now in progress along this line.

STATE COLLEGE OF KENTUCKY,
LEXINGTON, NOVEMBER, 1895.

THE SPECIFIC GRAVITIES OF WATER SOLUTIONS OF FORMIC ACID.

BY GEORGE M. RICHARDSON AND PIERRE ALLAIRE.

Having frequent occasion to determine the approximate amount of acid in formic acid solutions, we have prepared the following table. The specific gravities were determined by the use of a picnometer at 20° C. The amount of acid in the various solutions was determined by titrating with a standard solution of sodium hydroxide, with phenolphthalein as an indicator. Pure anhydrous formic acid was prepared in the usual manner from recrystallized lead formate and dry hydrogen sulphide, and the acid thus obtained was redistilled over dry lead formate. Formic acid was finally obtained which gave 100 per cent. acid upon titration with the standard alkali. This acid was found to have a specific gravity of 1.2213 at 20° C. (water at 4° C. = 1). The anhydrous acid was then diluted by the addition of measured amounts of distilled water, the specific gravity and the amount of acid in each solution being determined. In this manner seventy-one determinations were made at regular intervals between the pure acid and a dilute solution containing only 0.618 per cent. acid.

From the data thus obtained the following table was calculated :

Specific Gravities of Mixtures of Formic Acid and Water at 20° C. Water at 4° C. = 1.

Specific gravity of mixture.	Per cent. of formic acid by weight.	Per cent. of formic acid by volume.	Specific gravity of mixture.	Per cent. of formic acid by weight.	Per cent. of formic acid by volume.
0.9983	0.00	0.00	1.0941	39.00	34.92
1.0020	1.00	0.82	1.0964	40.00	35.90
1.0045	2.00	1.64	1.0991	41.00	36.88
1.0071	3.00	2.48	1.1016	42.00	37.89
1.0094	4.00	3.30	1.1039	43.00	38.85
1.0116	5.00	4.14	1.1063	44.00	39.86
1.0142	6.00	4.98	1.1086	45.00	40.82
1.0171	7.00	5.81	1.1109	46.00	41.83
1.0197	8.00	6.68	1.1131	47.00	42.82
1.0222	9.00	7.55	1.1158	48.00	43.88
1.0247	10.00	8.40	1.1186	49.00	44.91
1.0272	11.00	9.26	1.1208	50.00	45.88
1.0297	12.00	10.14	1.1224	51.00	46.87
1.0322	13.00	11.03	1.1245	52.00	47.89
1.0346	14.00	11.96	1.1270	53.00	48.93
1.0371	15.00	12.80	1.1296	54.00	49.97
1.0394	16.00	13.68	1.1321	55.00	51.01
1.0418	17.00	14.48	1.1343	56.00	52.02
1.0442	18.00	15.38	1.1362	57.00	53.04
1.0465	19.00	16.29	1.1382	58.00	54.07
1.0489	20.00	17.17	1.1402	59.00	55.09
1.0513	21.00	18.06	1.1425	60.00	56.13
1.0538	22.00	18.97	1.1449	61.00	57.16
1.0562	23.00	19.88	1.1474	62.00	58.26
1.0586	24.00	20.81	1.1494	63.00	59.30
1.0610	25.00	21.73	1.1518	64.00	60.35
1.0634	26.00	22.63	1.1544	65.00	61.44
1.0657	27.00	23.53	1.1566	66.00	62.51
1.0682	28.00	24.47	1.1585	67.00	63.57
1.0706	29.00	25.42	1.1605	68.00	64.62
1.0730	30.00	26.37	1.1629	69.00	65.71
1.0754	31.00	27.28	1.1656	70.00	66.80
1.0778	32.00	28.20	1.1678	71.00	67.90
1.0801	33.00	29.19	1.1703	72.00	68.99
1.0824	34.00	30.13	1.1729	73.00	70.10
1.0848	35.00	31.10	1.1753	74.00	71.21
1.0872	36.00	32.05	1.1770	75.00	72.27
1.0896	37.00	32.98	1.1786	76.00	73.34
1.0920	38.00	33.97	1.1802	77.00	74.38

Specific gravity of mixture.	Per cent. of formic acid by weight.	Per cent. of formic acid by volume.	Specific gravity of mixture.	Per cent. of formic acid by weight.	Per cent. of formic acid by volume.
1.1819	78.00	75.47	1.2045	90.00	88.74
1.1838	79.00	76.58	1.2060	91.00	89.84
1.1861	80.00	77.67	1.2079	92.00	91.00
1.1877	81.00	78.81	1.2100	93.00	92.13
1.1897	82.00	79.92	1.2118	94.00	93.22
1.1915	83.00	80.97	1.2141	95.00	94.48
1.1930	84.00	82.06	1.2159	96.00	95.57
1.1954	85.00	83.19	1.2171	97.00	96.63
1.1977	86.00	84.32	1.2184	98.00	97.76
1.1995	87.00	85.45	1.2203	99.00	98.93
1.2013	88.00	86.54	1.2213	100.00	100.00
1.2029	89.00	87.64			

Some idea of the contraction in volume that takes place when formic acid and water are mixed may be gained from the following table.

The first column gives the per cent. by weight of acid in the mixture; the second column gives the actual specific gravity of the mixture; the third column gives the specific gravity such a mixture would have were there no change in volume; the fourth column gives, in cubic centimeters, the contraction that takes place when enough anhydrous acid and water are brought together to make 100 cc. of the mixture.

Per cent. by weight of formic acid in mixture.	Actual specific gravity of mixture.	Calculated specific gravity if no volume change.	Contraction in cc.
10.00	1.0247	1.0168	0.78
20.00	1.0489	1.0361	1.23
30.00	1.0730	1.0561	1.60
40.00	1.0964	1.0769	1.81
50.00	1.1208	1.0986	2.02
60.00	1.1425	1.1211	1.90
70.00	1.1656	1.1446	1.83
80.00	1.1861	1.1691	1.45
90.00	1.2045	1.1946	0.82

STANFORD UNIVERSITY, CAL.,
JUNE 23, 1896.

THE CONSTITUTION OF BENZANILIDE.

By N. Knight.

The uncertainty in regard to the constitution of benzanilide suggested the experiments described in this paper. Lack of time prevented me from pursuing the investigation farther than herein indicated and, although the results do not justify the drawing of any important conclusion in regard to the constitution of benzanilide, they are of some interest, and may be of service to some future investigator. Just as benzamide may have the structure $C_6H_5.C\begin{matrix}\diagup NH_2\\ \diagdown O\end{matrix}$ or $C_6H_5.C\begin{matrix}\diagup OH\\ \diagdown NH\end{matrix}$, so the anilide may have the structure, $C_6H_5.C\begin{matrix}\diagup NHC_6H_5\\ \diagdown O\end{matrix}$, or $C_6H_5.C\begin{matrix}\diagup OH\\ \diagdown NC_6H_5\end{matrix}$. If the first of these two formulas is correct, then, apparently, the same product should result whether the sulphanilide is treated with benzoyl chloride, or benzanilide is treated with benzenesulphonchloride:

1. $C_6H_5.SO_2.N\begin{matrix}\diagup H\\ \diagdown C_6H_5\end{matrix} + C_6H_5.C\begin{matrix}\diagup Cl\\ \diagdown O\end{matrix} =$

$$C_6H_5.C(=O)-N(C_6H_5)-SO_2.C_6H_5 + HCl;$$

2. $C_6H_5.SO_2.Cl + C_6H_5-C(=O)-NHC_6H_5 =$

$$C_6H_5-C(=O)-N(C_6H_5)-SO_2.C_6H_5 + HCl.$$

If the second formula above given for benzanilide is correct, then the products formed in these reactions should apparently be different:

1. $C_6H_5.C(OH)=NC_6H_5 + C_6H_5.SO_2Cl =$

$$C_6H_5.C(O.SO_2C_6H_5)=NC_6H_5 + HCl;$$

$$2.\ C_6H_5.SO_2.N\begin{matrix}H\\ C_6H_5\end{matrix} + C_6H_5.C\begin{matrix}Cl\\ O\end{matrix} =$$

$$C_6H_5.SO_2.N\begin{matrix}CO.C_6H_5\\ C_6H_5\end{matrix} + HCl.$$

So much for speculation. As a matter of fact the reactions do not take place as it was thought they might.

Twelve grams benzenesulphanilide was mixed with 8 grams benzoyl chloride and the mixture in a test-tube immersed in a sulphuric-acid bath, the temperature of which was gradually raised. At 110° there was a copious evolution of hydrochloric acid, which ceased at 140°. The mixture was further heated to 180°, and kept at that temperature for ten hours. The cooled mass was a red, brittle solid of vitreous luster, breaking with a conchoidal fracture. It was easily soluble in dilute alcohol. By dissolving in alcohol and adding water in sufficient quantity, there separated from the solution a reddish, thick, oily substance, which was easily removed. On standing a few days, a white substance crystallized from the solution. This was purified by repeated crystallizations from alcohol, and was found to melt at 151°. Attempts to purify the oily portions were fruitless. The crystals were analyzed with the following results, which show that the substance is dibenzoylanilide, $\begin{matrix}C_6H_5CO\\ C_6H_5CO\end{matrix}\!>\!NC_6H_5$:

	Calculated for $C_{20}H_{15}NO_2$.	Found. I.	Found. II.
C	79.73	80.19	80.01
H	4.98	5.17	5.15
N	4.65	4.41	4.48

There is some uncertainty as regards the true melting-point of dibenzoylanilide, as different experimenters give different points. A consideration of the properties of the substance and of the results obtained by analyzing it, leave little doubt in regard to its identity. How it can be formed under the conditions described is another question. This will be briefly discussed farther on.

Reversing the order, 9 grams benzenesulphonchloride was mixed with 8.5 grams benzanilide, and the mixture heated as

in the first experiment. In general, the same phenomena were observed, and a similar reddish solid was formed. This was treated with alcohol and water, and a white, crystalline substance was obtained. This, like the substance obtained in the first experiment, melted at 151°, and the analysis showed that it had the same composition.

In both experiments a second compound was obtained, which, on purification, proved to be the aniline salt of benzenesulphonic acid, $C_6H_5.SO_2ONH_3C_6H_5$. It appeared in the form of beautiful white crystals, which melted at 231°, and, on analysis, gave the following results :

	Calculated for $C_{12}H_{13}SNO_3$.	Found. I.	II.
C	57·37	57·58	57·28
H	5.18	4.83	....
S	12.75	....	....
N	5.58	....	....

The salt was prepared by bringing benzenesulphonic acid and aniline together, and it was found to be identical with that obtained as above indicated.

Other by-products were formed in both experiments, but in quantities insufficient for a satisfactory examination. The most definite of these was a substance crystallizing in plates, that melted at 212°. It was not always observed.

How can dibenzoylanilide be formed in the experiments described? It seems possible that in the first experiment the principal reactions are these :

1. $C_6H_5.COCl + C_6H_5.NH.SO_2.C_6H_5 = \begin{matrix} C_6H_5.CO \\ C_6H_5.SO_2 \end{matrix}\!>\!NC_6H_5 + HCl$;

2. $\begin{matrix} C_6H_5.CO \\ C_6H_5.SO_2 \end{matrix}\!>\!NC_6H_5 + C_6H_5COCl = \begin{matrix} C_6H_5.CO \\ C_6H_5.CO \end{matrix}\!>\!NC_6H_5 + C_6H_5.SO_2Cl.$

In the second experiment the principal changes may be those represented below :

1. $C_6H_5.CO.NHC_6H_5 + C_6H_5SO_2Cl = \begin{matrix} C_6H_5.C{-}NC_6H_5 \\ \quad\quad >O \\ C_6H_5.C{-}NC_6H_5 \end{matrix} + C_6H_5.SO_2OH + HCl.$

$$2.\quad \begin{matrix} C_6H_5.C{-}NC_6H_5 \\ \quad\quad >O \\ C_6H_5.C{-}NC_6H_5 \end{matrix} + H_2O + C_6H_5.SO_2OH =$$
$$\begin{matrix} C_6H_5.CO \\ C_6H_5.CO \end{matrix}\!\!>NC_6H_5 + C_6H_5.SO_2NH_2C_6H_5.$$

REVIEWS.

TRAITÉ DE CHIMIE ORGANIQUE D'APRÈS LES THÉCRIES MODERNES: par AUGUSTE BÉHAL, Professeur agrégé à l'École supérieure de Pharmacie de Paris, Pharmacien en chef de l'Hôpital Ricord, Lauréat de l'Institut, Secrétaire général de la Société chimique, etc. Précéde d'une Préface de M. CH. FRIEDEL, Membre de l'Institut. Tome Premier, avec 36 Figures dans le Texte. Paris: Octave Doin, Éditeur. 1896. 963 pp. Price, 30 francs ($6.00).

This book has been honored by special mention in a recent meeting of the German Chemical Society, a fact which will no doubt attract much attention to it. That Professor Friedel has been willing to write a preface for it is additional evidence in its favor. To be sure this preface consists mostly of a reply to Ostwald's article on Atoms, that stirred up the physicists and chemists so deeply last year, but what M. Friedel says of M. Béhal's book is most complimentary: "Ceux qui liront le livre que j'ai l'honneur de présenter au public, et qui se recommande par luimême, étant le résultat d'un enseignement de six années fait à l'École supérieure de pharmacie de Paris, comprendront facilement combien il serait vain et illusoire de supprimer les hypothèses et les symboles qui servent en chimie à enchaîner les faits, à représenter les transformations, à soutenir la mémoire sans mettre à leur place quelque chose de plus satisfaisant. Ces hypothèses et ces symboles ont été et sont chaque jour des guides fidèles dans la découverte de faits nouveaux, et personne ne pourrait contester l'action puissante qu'ils ont exercée pour le progrès de la chimie.

"M. Béhal, qui a eu le mérite d'introduire le premier la notation et, ce qui vaut mieux, les idées atomiques dans l'enseignement de l'École de pharmacie, et qui est non seulement un professeur plein d'entrain mais un chercheur habile et heureux, a su donner à son livre ce double caractère theorique et pratique."

The chief characteristic of the book is its clear systematic arrangement. Nothing could be better. The text is also clear, readable, and interesting. It is difficult, however, to see to what class of students the book is addressed. It cannot be intended for beginners, for the first 200 pages deal with matters that cannot be understood until some knowl-

edge of the compounds of carbon has been acquired. On the other hand, the accounts of methods of determining constitution are often so detailed and elementary as to indicate that they cannot be intended for advanced students. The book is, in fact, of intermediate grade, and is well calculated to be of assistance to those who have already studied organic chemistry to some extent. A feature of the book that will commend it to some is the use of the new nomenclature adopted by the Geneva Congress in 1892. There is no other book except Beilstein in which the new nomenclature is used systematically, and yet, judging by the recent numbers of the journals of chemistry, it is time that chemists should familiarize themselves with it, as it is certainly coming into more and more common use. We English-speaking chemists are going to have a hard time of it with the suffixes *ane*, *ene*, and *ine*. We can't pronounce *ene* ān̄e without running afoul of *ane*, nor can we pronounce it ean without danger of confusion with *ine*. We might, to be sure, give *ine* the long ī, but that is not in accordance with custom. There are difficulties in the way, plainly.

References to the journals of chemistry are rarely given, though the names of chemists are frequently given. French names predominate. They are often given when the relative importance of the subjects does not appear to call for their mention. On the other hand, great names are omitted in some cases. For example, Bunsen is not mentioned in connection with cacodyl compounds, while Meunier, Bourquelot, Villiers and Fayolle, Jungfleisch, Maquenne, and other French names are found at every turn. This is, in a way, a small matter, and does not to any extent lessen the value of the book, which may be cordially recommended to American students. I. R.

ANALYTICAL CHEMISTRY. By N. MENSCHUTKIN, Professor in the University of St. Petersburg. Translated from the third German edition under the supervision of the author, by JAMES LOCKE. Part I, Qualitative Analysis. New York: MacMillan. 1896. 294 pp.

Menschutkin's is perhaps the best in every respect of the larger text-books on this subject. It is certainly the best for study. The general discussions of reactions of groups of elements, and the study of single elements, make everything clear and logical to the student who has learned to think chemically, and it is intended only for such. The author rightly protests against teaching analysis to those who have not studied general chemistry. Qualitative analysis becomes clear and interesting under Menschutkin's guidance, and the translation, which is good, should be welcomed. E. R.

RECHERCHES SUR LA CONGELATION DES SOLUTIONS AQUEUSES ÉTENDUES. Par M. A. PONSOT, ancien élève de l'École normale speciale, Agrégé de l'enseignement secondaire spécial, Docteur ès-sciences. Gauthier-Villars et Fils. Paris. 1896. pp. 114.

In the first chapter of this book the author has given a brief review of the work which has been done on the lowering of the freezing-point of a solvent by the dissolved substance. The Law of Blagden, the work of Rüdorff, Coppet, and especially that of Raoult, are considered. The paper of van't Hoff, showing the analogies between dilute solutions and gases, is discussed, and its relation to the Arrhenius theory of electrolytic dissociation referred to; a theory which the author thinks is by no means supported by the experimental results.

Ponsot then takes up his own experimental investigations along this line, which consist in determining, by a new method, the lowering of the freezing-point of water, produced by solutions of sodium chloride, potassium chloride, barium chloride, calcium chloride, potassium sulphate, sulphuric acid, lead acetate, cane sugar, acetic and oxalic acids. He compares his own results in each case with those of the other investigators who have worked on these same substances, by means of curves. The *source of error* in the work of *all* the other experimenters is pointed out with not a little confidence.

Arrhenius' results are too large because his freezing-mixture was too cold. Raoult found lowerings which were too great because his refrigerating-bath was also too cold, and radiation was not entirely prevented. Jones's results are apparently affected by the same source of error. In the work of Loomis radiation came into play and affected his results considerably. The correction, which Nernst and Abegg applied, makes their results more nearly coincident with the true values, which are those found by Ponsot.

Perhaps the most interesting part of the second half of the book, which is theoretical, is that which deals with the theory of electrolytic dissociation. If this theory is true, electrolytes, at extreme dilutions, must be completely broken down into their ions. These would then lower the freezing-point of the solvent to the same extent. We have not enough data to decide whether the first point is true, but the work of Ponsot has shown that the limit of the molecular-lowering varies with the substance employed, and therefore the Arrhenius' theory of electrolytic dissociation must be abandoned. It is a matter of deep regret that Ponsot did not inform himself a little more carefully in reference to some of the experimentally established facts. On page 10 we learn that "the values of i obtained from the freezing-point method, and from conduc-

tivity are of the same order of magnitude, but coincide rarely. For the substances which Arrhenius calls regular these differences may become 15 to 20 per cent; for the others, 70 to 80 per cent.'' This is used as an argument against the dissociation theory. Had Ponsot consulted the recent work of Jones' he would have found that these differences are, in general, somewhat smaller. Below are given a few of the values of the dissociation of different types of electrolytes as calculated from the freezing-point results of Jones, and from the conductivity determinations of Kohlrausch. The dissociation coefficient α, as calculated from freezing-point lowerings is equal to $i-1$ for binary electrolytes, and $\frac{i-1}{2}$, for ternary. The well-known method of calculating α from conductivity results is $\alpha = \frac{\mu_v}{\mu_\infty}$, in which μ_v is the molecular conductivity at volume v, and μ_∞ at infinite dilution.

Compounds.	Concentration. Gram-molecular, normal.	Kohlrausch's results from conducticity.	Jones's results from freezing-point lowerings.
		Per cent.	Per cent.
NaCl, $\mu_\infty = 1029$	0.001	98.0	98.4
"	0.01	93.5	90.5
"	0.1	84.1	84.1
$BaCl_2$, $\mu_\infty = 1144$	0.001	93.9	94.2
"	0.005	87.9	87.6
"	0.05	75.3	77.7
H_2SO_4, $\mu_\infty = 3342$	0.003	89.8	86.0
"	0.005	85.4	83.8
"	0.05	62.3	60.7
NaOH, $\mu_\infty = 1880$	0.002	98.9	98.4
"	0.01	99.5	93.7
"	0.05	90.4	88.4

Reference to the original paper will show that the comparison from which the above table was taken, was made for seven salts, four acids, and three bases, with results nearly as concordant throughout as the above. In the light of these facts, the full significance of the point raised by Ponsot is not quite apparent.

The question of the effect of radiation seems to have been settled satisfactorily by Raoult,[2] with the result that in the form of apparatus ordinarily employed, it is too small to consider. So much the more could it be left out of account,

[1] Phil. Mag. [5], **36**, 483.

[2] Revue Scientifique, (Paris), 1894, **2**, 321.

where the volume of the solution was large, which was true for the first time in the apparatus employed by Jones.

But the objection offered by Ponsot to the dissociation theory, which it is most difficult to understand, is the last named, that the molecular-lowering at great dilution should be a constant for different substances. This would be true, in terms of the dissociation theory, only when the molecules of the different compounds dissociated into the same number of ions. The experimental work of Ponsot does not appear to bear very strongly upon this point, for the obvious reason that *he has not worked at all with very dilute solutions.*

Reference to the work of Kohlrausch[1] on conductivity, or of Jones[2] on freezing-point lowerings, will show that many of the electrolytes which Ponsot employed are not completely dissociated at the greatest dilution with which he worked. The theory of dissociation seems thus to be taxed beyond its legitimate obligations.

Were complete references to the literature given in the text itself, instead of a very imperfect list at the end of the volume, the convenience of the reader would have been met rather more satisfactorily.

Finally, since the dissociation theory must now be relegated to history, it is at least unfortunate that Ponsot did not explain why the molecular-lowering, calculated from his own results, increases with the dilution; for potassium sulphate from 4.141 to 4.624, for sulphuric acid from 4.183 to 4.576, and for lead acetate from 3.708 to 4.608. HARRY C. JONES.

KURZES LEHRBUCH DER ORGANISCHEN CHEMIE von Professor DR. A. BERNTHSEN, Vorstand des Hauptlaboratoriums der Badischen Anilin- und Soda-Fabrik, Ludwigshafen am Rhein, früher Professor an der Universität zu Heidelberg Sechste Auflage, bearbeitet in Gemeinschaft mit DR. EDWARD BUCHNER, Professor an der Universität zu Tübingen. Braunschweig: Druck and Verlag von Friedrich Vieweg und Sohn. 1896.

The second edition of the English translation of this excellent book has already been recently reviewed in This JOURNAL (**17**, 204), so that it will only be necessary here to call attention to the changes and improvements made in this edition of the work.

The high character of the previous editions has been maintained, and the author is to be congratulated in having associated with himself in the revision of the book such an experienced teacher as Professor Buchner, of the University of Tübingen. Corrections and additions have been made, where they were necessary, to bring the book up to date, and in some cases this has necessitated a complete revision of a few

[1] Ann. der Phys. Wied., **26**, 161. [2] Ztschr. phys. Chem., **11**, 110, 529; **12**, 623.

chapters, like those on the acid derivatives, the sugars, the terpenes, etc. All of the excellent features of the former editions have been retained in this edition, and a much fuller and better index has been specially prepared for it by Herr Dinard.

The book is almost universally used throughout Germany by those studying organic chemistry, and its popularity is attested by the fact that it has already gone through six editions in nine years. It contains just what a student of the subject wants to know without being either too full or too brief. The most recent work on the various subjects is given together with the latest theoretical views, but in every case the evidence on which these views is based is also given.

As a text-book of organic chemistry there is no book to compare with it, though it must be said that it is too full to put into the hands of beginners in the subject. For those, who already have some knowledge of organic chemistry, and who wish to supplement this knowledge and to know the latest development of the science, this book will undoubtedly be most valuable. W. R. O.

STUDIES IN CHEMICAL DYNAMICS. By J. H. VAN 'T HOFF. Revised and enlarged by DR. ERNST COHEN. Translated by THOMAS EWAN, M.Sc., Ph.D. Easton: Chemical Publishing Co.; and London: Williams & Norgate. 286 pp. 8 vo.

The appearance of this new revised and enlarged edition of van 't Hoff's *Etudes de Dynamique Chimique*, and of its English translation may well be subjects of congratulation to every one interested in the progress of general chemistry. The work still retains the form of the original edition and contains almost all of the material presented in it. It has been extended mainly by the inclusion of the numerous recent investigations carried out in van 't Hoff's laboratory, so that, as stated in the preface, it is a historical record of the work done in that laboratory. It possesses, therefore, rather the character of a scientific monograph than that of an introductory text-book; and, when used for purposes of instruction, the fact should be borne in mind that there are some important principles in regard to chemical change and equilibrium, and many important applications which are not considered in this work. As examples of these may be mentioned catalytic actions and the numerous applications of the electrolytic dissociation theory to the phenomena of equilibrium.

The book is, however, especially valuable as an original contribution to science and as an aid to the scientific investigator, for the results of many hitherto unpublished researches are presented in it, and most of the matters consid-

ered are treated in much detail. About one-half of the book is devoted to the laws governing the rate of chemical change, and the remaining half to a discussion of chemical equilibrium and of the measurement of chemical affinity. The most important additions of a general character to the original edition are a table of experiments illustrating the remarkable principle, recently discovered, that the effect of temperature on the speed of all reactions is of the same order of magnitude, a deduction of the thermo-dynamical relation between temperature and the equilibrium constant, and a detailed discussion of the methods of determining the transition temperature.

A. A. NOYES.

THE CHEMICAL ANALYSIS OF IRON.—A Complete Account of all the best known methods for the Analysis of Iron, Steel, Pig-Iron, Iron Ore, Limestone, Slag, Clay, Sand, Coal, Coke, and Furnace and Producer Gases. By ANDREW ALEXANDER BLAIR. Third Edition. Philadelphia: J. B. Lippincott Co. 1896.

The favor with which Blair's Chemical Analysis of Iron was received when the first edition was published eight years ago was due to the fact that the methods of analysis described in the book were largely the result of the actual experience of a chemist of extensive practice in this special line of work. The directions were minute, so that no one need go astray in his work, and they bore, moreover, the distinct stamp of the author's personality.

In the subsequent editions of the book the author has kept well within the bounds originally established in the first edition and has not attempted to give all the new iron and steel processes which have been proposed during recent years. If he had done this his book would have become unwieldy in size and lost much of its usefulness in losing its strong individuality. The third edition contains, in addition to minor changes in the direction of greater accuracy, a few new and approved processes, and also the preliminary report of the Subcommittee on Standards of the International Steel Standard Committee on the Volumetric Determination of Phosphorus in Steel. Many years of work by five chemists of great experience in iron and steel analysis are represented in this report which is put forward tentatively to invite comment and criticism. The practice in the laboratories of iron and steel works in this country is undoubtedly the best in the world in respect to accuracy and rapidity, and it has been with these two ends in view that the committee has been working. Mr. Blair, as a member of this committee, has done a large amount of work both in determining the composition of the ammonium phospho-molybdate precipitate and also in devising useful modifications of the process and apparatus.

In an appendix there is a description of a rapid and accurate method of determining nickel and aluminum in steel by Mr. Chase of the Midvale Steel Works.

The third edition of this standard work will receive the same cordial welcome from chemists and teachers as its predecessors. It has become indispensable to all who work in the chemistry of iron. THOMAS M. DROWN.

GAS AND FUEL ANALYSIS FOR ENGINEERS. A compend for those interested in the economical application of fuel. Prepared especially for the use of students at the Massachusetts Institute of Technology. By AUGUSTUS H. GILL, S.B., Ph.D. Assistant Professor of Gas Analysis. 89 pages. New York: John Wiley and Sons. 1896.

This book will be especially welcome to instructors in engineering schools since there is no other single small book covering the same ground. The topics considered are sampling, gas apparatus of Orsat, Bunte, and Elliott, measurement of temperature, calculation of air required to burn a fuel and loss of heat in flue gases, reagents, derivation, and composition of fuels, methods of analysis, and determination of heating value. Under the last head the Mahler bomb and Junker gas calorimeter are described and detailed directions given for their use.

The discussion of the topics is as satisfactory as could be expected in so small a book and but few mistakes have been noticed. There is, perhaps, too great a tendency to take data from various sources and insert them bodily without recalculation or verification and without putting the data in different parts of the book into forms which are consistent with each other.

The statement of the method of calculating the results of Berthier's test is not clear, and there should have been the further statement that the results obtained do not agree with the theory, and that the use of an empirical factor is necessary.

Instead of Lunge's formula for the calculation of the loss of heat in the flue gases, the following, which has been given by the writer to his students, gives a closer approximation and is simpler:

$$\text{Percentage loss} = (0.0111 + \frac{100 - \%CO_2}{\%CO_2} 0.00605)\ (t' - t).$$

This formula is independent of the composition of the coal, in practical use. W. A. N.